

**Comparison of the Carbon System Parameters at the Global CO₂ Survey Crossover
Locations in the North and South Pacific Ocean, 1990–1996**

Richard A. Feely, Marilyn F. Lamb, Dana J. Greeley, and Rik Wanninkhof

Additional Contributors (arranged alphabetically):
Robert H. Byrne, David W. Chipman, Andrew G. Dickson, Catherine Goyet,
Peter R. Guenther, Kenneth M. Johnson, Charles D. Keeling, Robert M. Key,
Frank J. Millero, Christopher L. Sabine, Taro Takahashi,
Douglas W. R. Wallace, Christopher D. Winn, and C. S. Wong

Prepared by Linda J. Allison and Dana C. Griffith
Carbon Dioxide Information Analysis Center

Environmental Sciences Division
Publication No. 4883

Contribution No. 1944 from NOAA/Pacific Marine Environmental Laboratory

Date Published: October 1999

Preparation funded by
Budget Activity Number KP 12 02 03 0

Published by the
Carbon Dioxide Information Analysis Center
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6335
managed by
LOCKHEED MARTIN ENERGY RESEARCH CORP.
for the
U.S. DEPARTMENT OF ENERGY
Environmental Sciences Division
Office of Biological and Environmental Research
under contract DE-ACO5-96OR22464

CONTENTS

	Page
LIST OF FIGURES	v
LIST OF TABLES	ix
INVESTIGATORS	xi
ABSTRACT	xv
1. INTRODUCTION	1
2. ANALYTICAL METHODS	3
3. RESULTS AND DISCUSSION	4
3.1 Statistical Methods	4
3.2 Cruise Results	8
4. CONCLUSIONS	15
5. REMOTE ACCESS TO DATA LISTED IN THIS REPORT	15
6. ACKNOWLEDGMENTS	16
7. REFERENCES	17
APPENDIX A	
PLOTS OF THE CROSSOVER COMPARISONS IN THE NORTH AND SOUTH PACIFIC	A-1

LIST OF FIGURES

Figure		Page
1	Global CO ₂ survey stations in the Pacific (1990–1996)	2
2	Absolute value of the mean difference of dissolved inorganic carbon (DIC) (CRM corrected) for the 41 crossover comparisons	13
A.1	Comparison of salinity, oxygen (O ₂), fugacity of CO ₂ (<i>f</i> CO ₂), and dissolved inorganic carbon (DIC) at 170° E and 66° S	A-3
A.2	Comparison of salinity and dissolved inorganic carbon (DIC) at 178° W and 32° S	A-4
A.3	Comparison of salinity and dissolved inorganic carbon (DIC) at 175° W and 32° S	A-5
A.4	Comparison of salinity, oxygen (O ₂), fugacity of CO ₂ (<i>f</i> CO ₂), and dissolved inorganic carbon (DIC) at 170° W and 67° S	A-6
A.5	Comparison of salinity, oxygen (O ₂), and dissolved inorganic carbon (DIC) at 170° W and 32° S	A-7
A.6	Comparison of salinity, oxygen (O ₂), total alkalinity (TAlk), pH, and dissolved inorganic carbon (DIC) at 170° W and 17° S	A-8
A.7a	Comparison of salinity, oxygen (O ₂), and total alkalinity (TAlk) at 170° W and 10° S	A-9
A.7b	Comparison of fugacity of CO ₂ (<i>f</i> CO ₂), pH, and dissolved inorganic carbon (DIC) at 170° W and 10° S	A-10
A.8a	Comparison of salinity, oxygen (O ₂), and total alkalinity (TAlk) at 170° W and 5° S	A-11
A.8b	Comparison of fugacity of CO ₂ (<i>f</i> CO ₂), pH, and dissolved inorganic carbon (DIC) at 170° W and 5° S	A-12
A.9a	Comparison of salinity, oxygen (O ₂), and total alkalinity (TAlk) at 170E W and 0°	A-13
A.9b	Comparison of fugacity of CO ₂ (<i>f</i> CO ₂), pH, and dissolved inorganic carbon (DIC) at 170E W and 0°	A-14
A.10	Comparison of salinity and dissolved inorganic carbon (DIC) at 152° W and 53° N	A-15
A.11	Comparison of salinity, oxygen (O ₂), fugacity of CO ₂ (<i>f</i> CO ₂), and dissolved inorganic carbon (DIC) at 150° W and 37° S	A-16

Figure		Page
A.12	Comparison of salinity, oxygen (O_2), and dissolved inorganic carbon (DIC) at 150°E W and 32° S	A-17
A.13	Comparison of salinity, oxygen (O_2), total alkalinity (TAlk), and dissolved inorganic carbon (DIC) at 150° W and 17° S	A-18
A.14	Comparison of salinity, oxygen (O_2), fugacity of CO_2 (fCO_2), and dissolved inorganic carbon (DIC) at 135° W and 53° S	A-19
A.15	Comparison of salinity, oxygen (O_2), and dissolved inorganic carbon (DIC) at 135°E W and 33° S	A-20
A.16	Comparison of salinity, oxygen (O_2), and dissolved inorganic carbon (DIC) at 135° W and 17° S	A-21
A.17	Comparison of salinity, oxygen (O_2), and dissolved inorganic carbon (DIC) at 135° W and 5° S	A-22
A.18	Comparison of salinity, oxygen (O_2), and dissolved inorganic carbon (DIC) at 135° W and 35° N	A-23
A.19	Comparison of salinity, oxygen (O_2), and dissolved inorganic carbon (DIC) at 135° W and 40° N	A-24
A.20	Comparison of salinity, oxygen (O_2), fugacity of CO_2 (fCO_2), and dissolved inorganic carbon (DIC) at 126° W and 67° S	A-25
A.21a	Comparison of salinity, oxygen (O_2), and total alkalinity (TAlk) at 110° W and 0°	A-26
A.21b	Comparison of fugacity of CO_2 (fCO_2) and dissolved inorganic carbon (DIC) at 110° W and 0°	A-27
A.22a	Comparison of salinity, oxygen (O_2), and total alkalinity (TAlk) at 110° W and 5° N	A-28
A.22b	Comparison of fugacity of CO_2 (fCO_2) and dissolved inorganic carbon (DIC) at 110° W and 5° N	A-29
A.23	Comparison of salinity, oxygen (O_2), fugacity of CO_2 (fCO_2), and dissolved inorganic carbon (DIC) at 103° W and 67° S	A-30
A.24	Comparison of salinity, oxygen (O_2), and dissolved inorganic carbon (DIC) at 103° W and 32° S	A-31
A.25	Comparison of salinity, oxygen (O_2), total alkalinity (TAlk), and dissolved inorganic carbon (DIC) at 103°E W and 17°E S	A-32
A.26	Comparison of salinity, oxygen (O_2), fugacity of CO_2 (fCO_2), and dissolved inorganic carbon (DIC) at 88° W and 67° S	A-33

Figure		Page
A.27	Comparison of salinity, oxygen (O_2), and dissolved inorganic carbon (DIC) at 88° W and 32° S	A-34
A.28	Comparison of salinity, oxygen (O_2), fugacity of CO_2 (fCO_2), and dissolved inorganic carbon (DIC) at 86° W and 55° S	A-35
A.29	Comparison of salinity, oxygen (O_2), and dissolved inorganic carbon (DIC) at 86° W and 17° S	A-36
A.30	Comparison of salinity, oxygen (O_2), fugacity of CO_2 (fCO_2), and dissolved inorganic carbon (DIC) at 86° W and 13° S	A-37

LIST OF TABLES

Table	Page
1 Summary of station locations and observing laboratories for the crossover locations in the North and South Pacific	5
2 Summary of number of comparisons of salinity, oxygen (O ₂), dissolved inorganic carbon (DIC), fugacity of CO ₂ (<i>f</i> CO ₂), total alkalinity (TAlk), and pH at the 30 crossover locations in the North and South Pacific	7
3 Summary of the comparison results for dissolved inorganic carbon (DIC) for each of the 41 crossover comparisons during the Global CO ₂ Survey in the Pacific	9
4 Summary of the comparison results for fugacity of CO ₂ (<i>f</i> CO ₂) for each of the 16 crossover comparisons during the Global CO ₂ Survey in the Pacific	10
5 Summary of the comparison results for total alkalinity (TAlk) for each of the 15 crossover comparisons during the Global CO ₂ Survey in the Pacific	11
6 Summary of the comparison results for pH for each of the 5 crossover comparisons during the Global CO ₂ Survey in the Pacific	11
7 The effect of constants on the calculation of fugacity of CO ₂ (<i>f</i> CO ₂) at 20°C	12

INVESTIGATORS

The authors and additional contributors along with their affiliations and addresses are listed below.

Authors:

Richard A. Feely
NOAA, Pacific Marine Environmental Laboratory (PMEL)
7600 Sand Point Way N.E.
Seattle, WA 98115-0070

Marilyn F. Lamb
NOAA, Pacific Marine Environmental Laboratory (PMEL)
7600 Sand Point Way N.E.
Seattle, WA 98115-0070

Dana J. Greeley
NOAA, Pacific Marine Environmental Laboratory (PMEL)
7600 Sand Point Way N.E.
Seattle, WA 98115-0070

Rik Wanninkhof
NOAA, Atlantic Oceanographic and Meteorological Laboratory (AOML)
4301 Rickenbacker Causeway
Miami, FL 33149

Additional Contributors:

Robert H. Byrne
Department of Marine Science, University of South Florida (USF)
140 7th Avenue South
St. Petersburg, FL 33701

David W. Chipman
Lamont-Doherty Earth Observatory (LDEO) of Columbia University
Climate/Environment/Ocean Division
Rt. 9W
Palisades, NY 10964

Andrew G. Dickson
Scripps Institution of Oceanography (SIO)
Marine Physical Laboratory
9500 Gilman Drive
University of California, San Diego
La Jolla, CA 92093

Catherine Goyet
Woods Hole Oceanographic Institution (WHOI)
Marine Chemistry and Geochemistry Department
360 Woods Hole Drive, MS 25
Woods Hole, MA 02543

Peter R. Guenther
Scripps Institution of Oceanography (SIO)
Geosciences Research Division 0220

9500 Gilman Drive
University of California, San Diego
La Jolla, CA 92093

Kenneth M. Johnson
DOE, Brookhaven National Laboratory (BNL)
Bldg. 318
Upton, NY 1197

Charles D. Keeling
Scripps Institution of Oceanography (SIO)
Geosciences Research Division
9500 Gilman Drive
University of California, San Diego
La Jolla, CA 92093

Robert M. Key
Department of Geosciences
Princeton University
Guyot Hall
Princeton, NJ 08544

Frank J. Millero
Rosenstiel School of Marine and Atmospheric Sciences (RSMAS)
University of Miami
4600 Rickenbacker Causeway
Miami, FL 33149

Christopher L. Sabine
NOAA, Pacific Marine Environmental Laboratory (PMEL)
7600 Sand Point Way N.E.
Seattle, WA 98115-0070

Taro Takahashi
Lamont-Doherty Earth Observatory (LDEO) of Columbia University
Climate/Environment/Ocean Division
Rt. 9W
Palisades, NY 10964

Douglas W. R. Wallace
DOE, Brookhaven National Laboratory (BNL)
Bldg. 318
Upton, NY 1197
(Now at: Abteilung Meereschemie
Institut für Meereskunde an der Universität Kiel
Düsternbrooker Weg 20
24105 Kiel, Germany)

Christopher D. Winn
University of Hawaii (UH)
Dept. of Oceanography
1000 Pope Rd.
Honolulu, HI 96822
(Now at: Marine Science Program
Hawaii Pacific University
45-045 Kamehameha Hwy
Kaneohe, HI 96744-5297)

C. S. Wong
Institute of Ocean Science (IOS)
9860 W. Saanich Rd.
Sidney, BC, V8L 4B2, Canada

ABSTRACT

Feely, R. A., M. F. Lamb, D. J. Greeley, and R. Wanninkhof. 1999. Comparison of the Carbon System Parameters at the Global CO₂ Survey Crossover Locations in the North and South Pacific Ocean, 1990–1996. ORNL/CDIAC-115. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, U.S.A. 74 pp.

As a collaborative program to measure global ocean carbon inventories and provide estimates of the anthropogenic carbon dioxide (CO₂) uptake by the oceans, the National Oceanic and Atmospheric Administration and the U.S. Department of Energy have sponsored the collection of ocean carbon measurements as part of the World Ocean Circulation Experiment and Ocean-Atmosphere Carbon Exchange Study cruises. The cruises discussed here occurred in the North and South Pacific from 1990 through 1996. The carbon parameters from these 30 crossover locations have been compared to ensure that a consistent global data set emerges from the survey cruises. The results indicate that for dissolved inorganic carbon, fugacity of CO₂, and pH, the agreements at most crossover locations are well within the design specifications for the global CO₂ survey; whereas, in the case of total alkalinity, the agreement between crossover locations is not as close.

1. INTRODUCTION

Human activity is rapidly changing the trace gas composition of the earth's atmosphere, apparently causing greenhouse warming from excess carbon dioxide (CO_2) along with other trace gas species, such as water vapor, chlorofluorocarbons (CFCs), methane, and nitrous oxide. These gases play a critical role in controlling the earth's climate because they increase the infrared opacity of the atmosphere, causing the planetary surface to warm. Of all the anthropogenic CO_2 that has ever been produced, only about half remains in the atmosphere; it is the "missing" CO_2 for which the global ocean is considered to be the dominant sink for the man-made increase. Future decisions on regulating emissions of "greenhouse gases" should be based on more accurate models that have been adequately tested against a well-designed system of measurements. Predicting global climate change, as a consequence of CO_2 emissions, requires coupled atmosphere/ocean/terrestrial biosphere models that realistically simulate the rate of growth of CO_2 in the atmosphere, as well as its removal, redistribution, and storage in the oceans and terrestrial biosphere. The construction of a believable present-day carbon budget is essential for the skillful prediction of atmospheric CO_2 and temperature from given emission scenarios.

The world's oceans, widely recognized to be the major long-term control on the rate of CO_2 increases in the atmosphere, are believed to be absorbing about 2.0 GtC yr^{-1} (nearly 30 to 40% of the annual release from fossil fuels). Our present understanding of oceanic sources and sinks for CO_2 is derived from a combination of field data, that are limited by sparse temporal and spatial coverage, and model results that are validated by comparisons with oceanic bomb ^{14}C profiles. CO_2 measurements taken on the World Ocean Circulation Experiment (WOCE) cruises, which began in 1990, have provided an accurate benchmark of the ocean inventory of CO_2 and other properties. These measurements were cosponsored by the National Oceanic and Atmospheric Administration (NOAA) and the U.S. Department of Energy (DOE) via the U.S. Joint Global Ocean Flux Study (JGOFS) Program. Investigators supported by these funding agencies have collaborated to examine data collected during the WOCE and Ocean-Atmosphere Carbon Exchange Study (OACES) cruises. This report addresses the consistency of oceanic carbon dioxide system parameters during 1990–1996 in the North and South Pacific.

The four parameters of the oceanic carbon dioxide system are dissolved inorganic carbon (DIC), fugacity of CO_2 ($f\text{CO}_2$), total alkalinity (TALK), and pH. This report compares the carbon system parameters, along with salinity and dissolved oxygen (O_2), against sigma theta (σ_t) where cruises overlapped throughout the Pacific Ocean basin. Similar comparisons have been made for oceanic carbon in the Indian Ocean (Johnson et al. 1998; Millero et al. 1998). Additional comparisons have also been made by Robert Key of Princeton University and may be viewed at <http://geoweb.princeton.edu/staff/Key/key.cross/crossover.html>. In addition, comparisons of nutrient data have been compiled (Gordon et al. 1998). The cruise data for this report will be made available through the OACES and the Carbon Dioxide Information Analysis Center (CDIAC) data management centers (see Sect. 5).

The Pacific Ocean cruises occurred from 1990–1996, and data have been compared at 30 locations where cruises overlapped in the North and South Pacific Ocean (Fig. 1). We do not address survey stations in the Pacific where no crossovers occurred. In addition, carbon and hydrographic data collected during some of the Pacific expedition cruises (i.e., P2, P12, and S4I) were not available in time for this report.

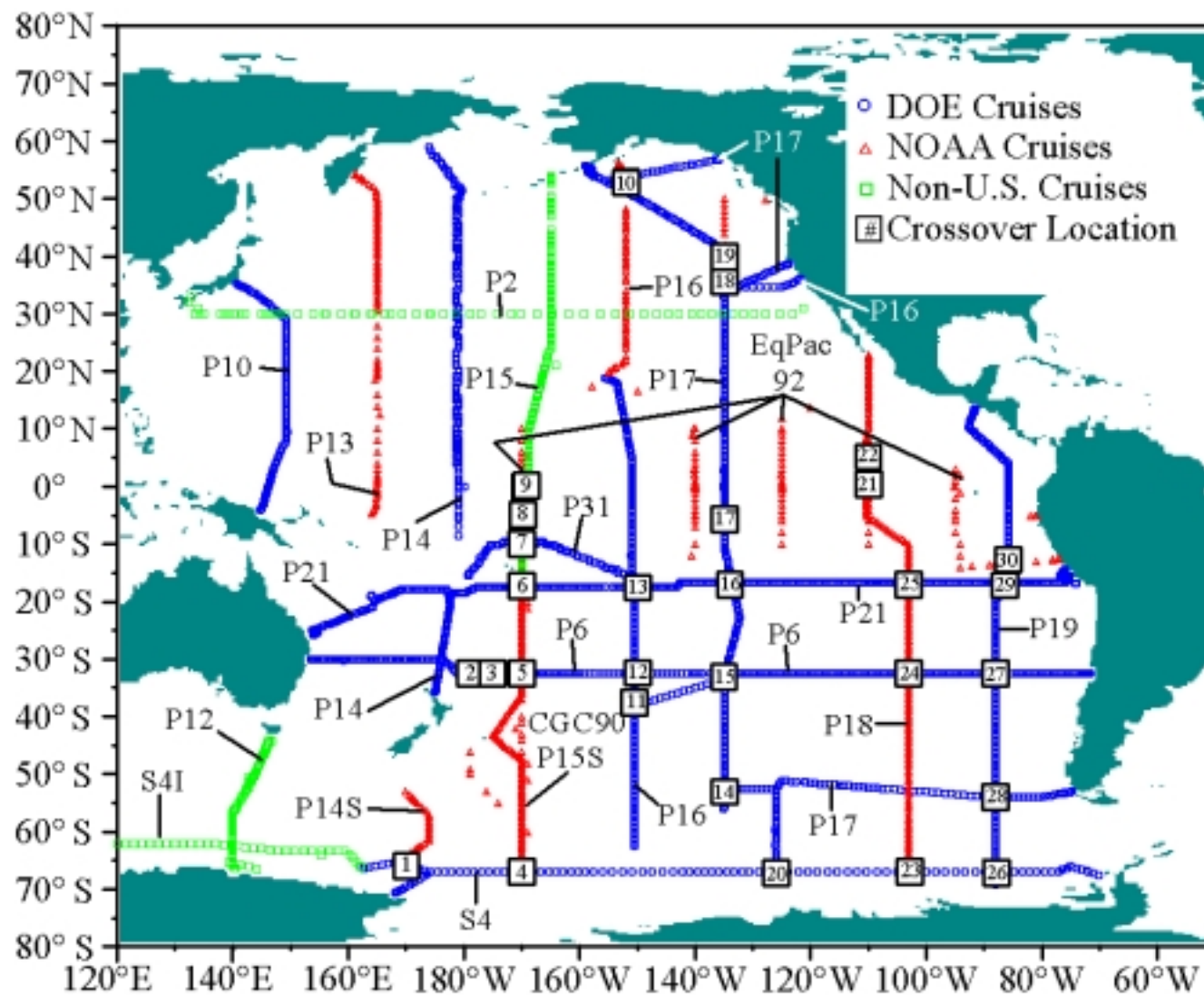


Fig. 1. Global CO₂ survey stations in the Pacific (1990–1996).

Location #/ Crossover Comparison	Nominal	
	Long.	Lat.
1 / 1	170°E	66°S
2 / 2	178°	32°S
3 / 3	175°	32°S
4 / 4	170°	67°S
5 / 5	170°	32°S
6 / 6	170°	17°S
7 / 7	170°	10°S
7 / 8	170°	10°S
7 / 9	170°	10°S
7 / 10	170°	10°S
8 / 11	170°	5°S
8 / 12	170°	5°S
8 / 13	170°	5°S
9 / 14	170°	0
9 / 15	170°	0
9 / 16	170°	0
10 / 17	152°	53°N
11 / 18	150°	37°S
12 / 19	150°	32°S
13 / 20	150°	17°S
13 / 21	150°	17°S
13 / 22	150°	17°S
14 / 23	135°	53°S
15 / 24	135°	33°S
16 / 25	135°	17°S
17 / 26	135°	6°S
18 / 27	135°	35°N
19 / 28	135°	40°N
20 / 29	126°	67°S
21 / 30	110°	0
21 / 31	110°	0
22 / 32	110°	5°N
22 / 33	110°	5°N
23 / 34	103°	67°S
24 / 35	103°	32°S
25 / 36	103°	17°S
26 / 37	88°W	67°S
27 / 38	88°W	32°S
28 / 39	86°W	55°S
29 / 40	86°W	17°S
30 / 41	86°W	13°S

2. ANALYTICAL METHODS

Analyses of all carbon parameters were performed following the techniques outlined in the *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water* (DOE 1994). Certified Reference Materials (CRMs) were used on all cruises as secondary standards for DIC, unless otherwise noted. Discussion of the preparation and use of CRMs is available in detail (UNESCO 1991; Dickson 1992; Dickson, Anderson, and Afghan, unpublished manuscript; Dickson, Afghan, and Anderson, unpublished manuscript). These materials consisted of a matrix of natural, sterile seawater. They were bottled in large batches into 500-mL borosilicate glass containers, sealed to prevent contamination, and shipped to the institutes participating in this study. These secondary standards were then analyzed at sea over the course of each of the cruises as a means to verify accuracy. Certification of the reference material for DIC is based on manometric analyses in the shore-based laboratory of Charles D. Keeling of Scripps Institution of Oceanography (SIO) over a period of several months (UNESCO 1991; Guenther 1994; Keeling, C. D., personal communication, 1999). Since CRMs were analyzed routinely for DIC during most cruises used in this report, all groups analyzing for TALK on those cruises subsequently analyzed CRMs as well; this enabled post-cruise corrections to be made to the TALK data based on archived samples that were analyzed at Dr. Keeling's laboratory at SIO. CRMs were not available for any other carbon parameter discussed in this report. Analyses of salinity and O₂ followed WOCE Hydrographic Program (WHP) protocol (WOCE 1994).

3. RESULTS AND DISCUSSION

3.1 Statistical Methods

Tables 1 and 2 summarize the crossover sites and parameters measured, and Tables 3–6 are summaries of the statistical data for each parameter at the crossover locations. Eleven laboratories from two countries participated in this comparison study that examines crossovers in both the North and South Pacific. At some of the crossover locations, the site was occupied on more than one occasion [i.e., the crossover at 170° W and 10° S was frequented by NOAA on three different cruises (CGC90, EqS92, and P15S), as well as by the Institute of Ocean Science (IOS) (P15N) and the University of Hawaii (UH) (P31)]. A total of 30 crossover locations were studied in this analysis and 41 individual crossover comparisons were made. Individual plots of each carbon parameter, along with salinity and O₂, were first created for every crossover against F₂ using data from the entire water column (Appendix A). Only data sets that showed good agreement in both salinity and O₂ data were used for the comparisons. An expanded area within the plot was examined further based on the region of reasonable agreement of the F₂ vs salinity plot. In most cases, F₂ \pm 27.0 was used in the expanded regions.

A curve-fitting routine was applied to the expanded plots (Appendix A) using a second-order polynomial fit (unless otherwise noted in Tables 3–6). The difference between each region of crossover was calculated based on evenly distributed intervals on the F₂ axis; the intervals chosen were, on average, 0.04 F₂ units apart. In the case where more than one station on a given cruise was computed at a particular crossover location, averages of the resulting fits of the two or more stations for that cruise were determined, and the total mean of the differences over the entire F₂ range was compared. This procedure was performed for every carbon parameter measured (Tables 3–6). The mean and standard deviation of the differences were computed, along with the mean and standard deviation of the absolute value of the differences. For the DIC data, the results were calculated both uncorrected and corrected using the CRMs as a basis for the corrections.

Table 1. Summary of station locations and observing laboratories for the crossover locations in the North and South Pacific

<u>Nominal position</u>		Cruise name/ WOCE line	Lead institute ^a	<u>Actual position</u>		CO ₂ parameters compared ^b	Date of occupation
Longitude	Latitude			Longitude	Latitude		
170° E	66° S	P14S	NOAA	171.03° E	66.02° S	<i>f</i> CO ₂ , DIC	17Jan1996
		S4	LDEO	169.99° E	65.88° S	<i>f</i> CO ₂ , DIC	26Mar1992
178E W	32E S	P6	BNL	177.67° W	32.50° S	DIC	02Jul1992
		P6	BNL	178.00° W	32.50° S	DIC	02Jul1992
		P6	BNL	178.28° W	32.50° S	DIC	02Jul1992
		P6	BNL	178.65° W	32.50° S	DIC	03Jul1992
		CGC90	NOAA	178.00° W	32.51° S	DIC	30Mar1990
		CGC90	NOAA	178.31° W	32.50° S	DIC	28Mar1990
		CGC90	NOAA	178.77° W	32.49° S	DIC	29Mar1990
175E W	32E S	P6	BNL	175.26° W	32.50° S	DIC	30Jun1990
		CGC90	NOAA	175.50° W	32.49° S	DIC	30Mar1990
170E W	67E S	P15S	NOAA	170.00° W	66.99° S	<i>f</i> CO ₂ , DIC	18Jan1996
		S4	LDEO	169.25° W	67.03° S	<i>f</i> CO ₂ , DIC	17Mar1992
170E W	32E S	P15S	NOAA	170.00° W	32.50° S	DIC	18Feb1996
		P6	BNL	173.17E W	32.50° S	DIC	29Jun1992
		P6	BNL	168.01E W	32.50° S	DIC	26Jun1992
170E W	17E S	P15S	NOAA	170.00E W	17.50° S	Talk, pH, DIC	26Feb1996
		P15S	NOAA	170.00E W	16.50° S	Talk, pH, DIC	27Feb1996
		P21	RSMAS	169.67E W	17.50° S	Talk, pH, DIC	30May1994
		P21	RSMAS	171.00E W	17.50° S	Talk, pH, DIC	31May1994
170E W	10E S	P15S	NOAA	169.63E W	9.93E S	DIC	01Mar1996
		P15S	NOAA	168.88E W	9.00E S	DIC	02Mar1996
		CGC90	NOAA	170.00E W	10.09E S	DIC	06Apr1990
		CGC90	NOAA	170.25E W	10.09E S	DIC	06Apr1990
170E W	10E S	P15S	NOAA	169.63E W	9.93E S	<i>f</i> CO ₂ , pH, DIC	01Mar1996
		P15S	NOAA	168.88E W	9.00E S	<i>f</i> CO ₂ , pH, DIC	02Mar1996
		EQS92	NOAA	169.99E W	10.01E S	<i>f</i> CO ₂ , pH, DIC	13Apr1992
170E W	10E S	P15S	NOAA	169.63E W	9.93E S	Talk, DIC	01Mar1996
		P15S	NOAA	168.88E W	9.00E S	Talk, DIC	02Mar1996
		P15N	IOS	168.90E W	10.03E S	Talk, DIC	05Nov1994
		P15N	IOS	169.00E W	9.01E S	Talk, DIC	05Nov1994
170E W	10E S	P15S	NOAA	169.63E W	9.93E S	Talk, pH, DIC	01Mar1996
		P15S	NOAA	168.88E W	9.00E S	Talk, pH, DIC	02Mar1996
		P31	UH	170.20E W	9.40E S	Talk, pH, DIC	12Feb1994
		P31	UH	170.55E W	9.40E S	Talk, pH, DIC	12Feb1994
170E W	5E S	P15S	NOAA	168.75E W	5.00E S	Talk, DIC	04Mar1996
		P15N	IOS	168.75E W	5.00E S	Talk, DIC	03Nov1994
170E W	5E S	P15S	NOAA	168.75E W	5.00E S	DIC	04Mar1996
		CGC90	NOAA	170.02E W	5.01E S	DIC	08Apr1990
170E W	5E S	P15S	NOAA	168.75E W	5.00E S	Talk, <i>f</i> CO ₂ , pH, DIC	04Mar1996
		EQS92	NOAA	169.98E W	5.01E S	Talk, <i>f</i> CO ₂ , pH, DIC	11Mar1992
170E W	0E	P15S	NOAA	168.75E W	0.00E	Talk, DIC	06Mar1996
		P15N	IOS	168.75E W	0.02E S	Talk, DIC	30Oct1994

Table 1 (continued)

Nominal position		Cruise name/ WOCE line	Lead institute ^a	Actual position		CO ₂ parameters compared ^b	Date of occupation
Longitude	Latitude			Longitude	Latitude		
170E W	0E	P15S	NOAA	168.75E W	0.00E	DIC	06Mar1996
		CGC90	NOAA	170.02E W	0.00E	DIC	09Apr1990
170E W	0E	P15S	NOAA	168.75E W	0.00E	<i>f</i> CO ₂ , pH, DIC	06Mar1996
		EQS92	NOAA	170.13E W	0.03E S	<i>f</i> CO ₂ , pH, DIC	09Mar1992
152E W	53E N	CGC91	NOAA	152.02E W	52.49E N	DIC	02Apr1991
		CGC91	NOAA	152.00E W	53.50E N	DIC	30Mar1991
		CGC91	NOAA	152.00E W	54.66E N	DIC	30Mar1991
		P16	WHOI	152.53E W	51.48E N	DIC	09Jun1993
		P16	WHOI	153.08E W	51.78E N	DIC	09Jun1993
		P16	WHOI	153.25E W	53.60E N	DIC	15Jun1993
		P16	WHOI	152.43E W	53.75E N	DIC	16Jun1993
		P16	WHOI	150.85E W	54.05E N	DIC	16Jun1993
150E W	37E S	P16	LDEO	150.50E W	37.49E S	<i>f</i> CO ₂ , DIC	12Aug1991
		P16	LDEO	150.48E W	37.49E S	<i>f</i> CO ₂ , DIC	12Oct1992
150E W	32E S	P6	BNL	149.83E W	32.50E S	DIC	19Jun1992
		P16	LDEO	150.50E W	32.50E S	DIC	19Jun1993
150E W	17E S	P16	WHOI/SIO	150.49E W	16.99E S	Talk, DIC	01Sep1991
		P21	RSMAS	149.17E W	17.50E S	Talk, DIC	12May1994
150E W	17E S	P21	RSMAS	150.08E W	17.50E S	Talk, DIC	21May1994
		P31	UH	149.60E W	17.20E S	Talk, DIC	26Jan1994
135E W	53E S	P17	LDEO	134.99E W	54.00E S	<i>f</i> CO ₂ , DIC	08Nov1992
		P17	LDEO	135.00E W	52.50E S	<i>f</i> CO ₂ , DIC	14Dec1992
135E W	33E S	P6	BNL	135.34E W	32.50E S	DIC	11Jun1992
		P17	LDEO	135.00E W	33.00E S	DIC	20Nov1992
135E W	17E S	P17	LDEO	133.37E W	17.83E S	DIC	29Jul1991
		P21	RSMAS	134.00E W	16.75E S	DIC	05May1994
135E W	5E S	P17	WHOI/SIO	135.00E W	5.00E S	DIC	06Jul1991
		P17	LDEO	135.00E W	6.00E S	DIC	21Jul1991
135E W	35E N	P17	WHOI	135.00E W	35.58E N	DIC	23May1993
		P17	WHOI	134.96E W	35.00E N	DIC	08Jun1991
135E W	40E N	CGC91	NOAA	135.00E W	40.00E N	DIC	22Feb1991
		P17	WHOI	135.00E W	40.50E N	DIC	28May1993
126E W	67E S	S4	LDEO	125.58E W	67.01E S	<i>f</i> CO ₂ , DIC	07Mar1992
		P17	LDEO	126.00E W	65.66E S	<i>f</i> CO ₂ , DIC	25Dec1992
110E W	0E	P18	NOAA	110.33E W	0.34E N	Talk, <i>f</i> CO ₂ , DIC	14Apr1994
		EQS92	NOAA	110.00E W	0.26E S	Talk, <i>f</i> CO ₂ , DIC	07Mar1992
110E W	0E	P18	NOAA	110.33E W	0.34E N	Talk, <i>f</i> CO ₂ , DIC	14Apr1994
		EQF92	NOAA	110.00E W	0.25E S	Talk, <i>f</i> CO ₂ , DIC	05Nov1992
110E W	5E N	P18	NOAA	110.34E W	5.00E N	Talk, <i>f</i> CO ₂ , DIC	17Apr1994
		EQS92	NOAA	109.93E W	5.02E N	Talk, <i>f</i> CO ₂ , DIC	04Mar1992
110E W	5E N	P18	NOAA	110.34E W	5.00E N	Talk, <i>f</i> CO ₂ , DIC	17Apr1994
		EQF92	NOAA	109.92E W	4.97E N	Talk, <i>f</i> CO ₂ , DIC	01Nov1992
103E W	67E S	P18	NOAA	103.01E W	67.00E S	<i>f</i> CO ₂ , DIC	27Feb1994
		P18	NOAA	103.00E W	66.50E S	<i>f</i> CO ₂ , DIC	27Feb1994
		S4	LDEO	101.84E W	66.99E S	<i>f</i> CO ₂ , DIC	02Mar1992
		S4	LDEO	105.17E W	66.99E S	<i>f</i> CO ₂ , DIC	03Mar1992

Table 1 (continued)

<u>Nominal position</u>		Cruise name/ WOCE line	Lead institute ^a	<u>Actual position</u>		CO ₂ parameters compared ^b	Date of occupation
Longitude	Latitude			Longitude	Latitude		
103E W	32E S	P18	NOAA	103.00E W	32.50E S	DIC	19Mar1994
		P6	BNL	103.30E W	32.50E S	DIC	19May1992
		P6	BNL	102.00E W	32.50E S	DIC	19May1992
103E W	17E S	P18	NOAA	103.00E W	17.00E S	TAlk, DIC	02Apr1994
		P18	NOAA	103.00E W	16.50E S	TAlk, DIC	03Apr1994
		P21	RSMAS	103.33E W	16.74E S	TAlk, DIC	20Apr1994
88E W	67E S	S4	LDEO	88.53E W	67.00E S	fCO ₂ , DIC	28Feb1992
		P19	LDEO	88.00E W	67.01E S	fCO ₂ , DIC	16Jan1993
88E W	32E S	P19	LDEO	87.99E W	32.50E S	DIC	13Mar1993
		P6	BNL	86.67E W	32.50E S	DIC	13May1992
		P6	BNL	87.33E W	32.50E S	DIC	13May1992
		P6	BNL	88.67E W	32.50E S	DIC	14May1992
86E W	55E S	P19	LDEO	88.01E W	53.99E S	fCO ₂ , DIC	1Mar1993
		P19	LDEO	87.99E W	54.02E S	fCO ₂ , DIC	10Jan1993
86E W	17E S	P19	LDEO	86.39E W	16.84E S	DIC	21Mar1993
		P21	RSMAS	86.70E W	16.75E S	DIC	4Nov1994
86E W	13E S	P19	LDEO	85.84E W	12.49E S	fCO ₂ , DIC	23Mar1993
		EQF92	NOAA	84.07E W	13.23E S	TAlk, fCO ₂ , DIC	25Nov1992
		EQF92	NOAA	86.80E W	13.43E S	TAlk, fCO ₂ , DIC	25Nov1992

^aLead Institutions:

BNL=Brookhaven National Laboratory

IOS=Institute of Ocean Sciences

LDEO=Lamont Doherty Earth Observatory

NOAA=National Oceanic and Atmospheric Administration

RSMAS=Rosenstiel School of Marine and Atmospheric Science

SIO=Scripps Institution of Oceanography

UH=University of Hawaii

WHOI=Woods Hole Oceanographic Institution

^bParameters compared:

DIC=dissolved inorganic carbon

fCO₂=fugacity of CO₂

TAlk=total alkalinity

pH

Table 2. Summary of the number of comparisons of salinity, oxygen (O₂), dissolved inorganic carbon (DIC), fugacity of CO₂ (fCO₂), total alkalinity (TAlk), and pH at the 30 crossover locations in the North and South Pacific

	Parameter					
	Salinity	O ₂	DIC	fCO ₂	TAlk	pH
Crossover comparisons	41	34	41	16	15	5

3.2 Cruise Results

The most detailed carbon parameter results are for DIC, as this parameter was measured on all of the cruises (Table 3). The next most frequently measured parameter was $f\text{CO}_2$, followed by TAlk and pH (Tables 4–6), respectively. DIC CRMs were available to the investigators for almost every cruise during the survey. In general, there is excellent agreement between DIC data sets at the crossover locations. At the beginning of the program, the goal was to obtain agreements between cruises that were less than 4.0 Fmol/kg. On 31 of 41 crossover comparisons the uncorrected DIC differences were less than this value, and on 24 of the comparisons the differences were less than 2.0 Fmol/kg.

Most of the cruises that did not meet this criteria occurred at the beginning of the program when methods were still being developed, and one comparison was during a strong El Niño event where the upper water column hydrography was significantly different from normal (Feely et al. 1995). When the DIC data were corrected for CRMs, 36 of the 41 comparisons were less than 4.0 Fmol/kg, and 31 comparisons were less than 2.0 Fmol/kg. The mean of the absolute value of the differences was 2.4 ± 2.8 Fmol/kg for the uncorrected data and 1.9 ± 2.3 Fmol/kg for the corrected data (Fig. 2). For a mean DIC concentration of approximately 2260 Fmol/kg in the deep Pacific, this difference is equivalent to an uncertainty of approximately 0.08%. The excellent agreement of the DIC data was likely due primarily to the use of the coulometer (UIC, Inc.) coupled with a SOMMA (Single Operator Multiparameter Metabolic Analyzer) inlet system developed by Ken Johnson (Johnson et al. 1985, 1987, 1993; Johnson 1992) of Brookhaven National Laboratory (BNL), as well as the use of CRMs as secondary standards during the cruises. The spirit of cooperation and close interactions among the scientists and technicians who were responsible for the measurements also contributed to the outstanding quality of the data set.

The crossover comparison of $f\text{CO}_2$ in seawater is not as straightforward as the comparison of the other carbon parameters because the measurement temperature for $f\text{CO}_2$ differs for different cruises. The comparison thus requires a temperature normalization, which is performed by using the carbonate dissociation constants, and measured DIC. For comparison purposes, all values were normalized to 20°C in this report. The normalization is dependent on the dissociation constant used. In this comparison, we used the constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987). An example of the effect of constants on the final comparison is given in Table 7 in which we use typical deep-sea DIC and $f\text{CO}_2$ values as found in the southeastern Pacific. Also included in the table are the $(f\text{CO}_2@20^\circ\text{C})/\text{DIC}$ values in Fatm/(Fmol/kg) to illustrate the sensitivity of discrete $f\text{CO}_2$ measurements relative to DIC in deep waters.

We analyzed 16 crossover comparisons for $f\text{CO}_2$, and observed differences ranging between –28.7 and 34 Fatm, excluding the large difference during the 1992 El Niño at 5° N, 110° W. The mean of the absolute value of the difference was 17.6 ± 16.3 Fatm. In deep water 10 Fatm of $f\text{CO}_2$ measured at 20°C is approximately equivalent to an uncertainty of 1.5 Fmol/kg DIC. Thus, with the possible exception of two or three crossover locations, the systematic differences in the $f\text{CO}_2$ data corresponded to a similar uncertainty to that of the majority of the DIC results. Since there were no CRMs available for $f\text{CO}_2$ during the Pacific expeditions, the analysts used their own compressed gas standards for the measurements. Some of the differences between the data sets may have resulted from systematic differences between standards and/or differences between methods employed.

Table 3. Summary of the comparison results for dissolved inorganic carbon (DIC) for each of the 41 crossover comparisons during the Global CO₂ Survey in the Pacific

Location number/ Crossover comparison	Nominal position		Cruise name/ WOCE line		Salinity between cruises	SD Salinity between cruises) O ₂ between cruises (Fmol/kg)	SD O ₂ between cruises) DIC (uncorrected)		SD DIC between cruises) DIC (CRM corr.)		SD DIC between cruises) ±SD CRM SIO-cruise (Fmol/kg)	
	Long.	Lat.	Cruise 1	Cruise 2	Cruise 1–2	between cruises	Cruise 1–2	between cruises	Cruise 1–2	Cruise 1–2	between cruises	Cruise 1–2	Cruise 1–2	between cruises	Cruise 1	Cruise 2
1 / 1	170°E	66°S	P14S ^a	S4	0.003	0.002	−1.0	0.2	−1.5	−0.7	0.8	−1.1±0.9	−0.9±1.8			
2 / 2	178°W	32°S	P6 ^a	CGC90	0.007	0.011	ND ^b	ND ^b	0.9	−0.5	4	0.6±1.9	3.0±2.5			
3 / 3	175°W	32°S	P6 ^a	CGC90	0.001	0.002	ND ^b	ND ^b	3.1	0.7	4.7	0.6±1.9	3.0±2.5			
4 / 4	170°W	67°S	P15S ^a	S4	0.005	0.002	−1.6	0.2	3.8	3.6	0.8	−1.1±0.9	−0.9±1.8			
5 / 5	170°W	32°S	P15S ^a	P6	0.000	0.001	−0.5	0.1	−0.3	−0.5	0.7	−1.1±0.9	0.6±1.9			
6 / 6	170°W	17°S	P15S ^a	P21	−0.007	0.001	−6	ND ^b	−1.5	−1.3	1.1	−1.1±0.9	0.9±1.1			
7 / 7	170°W	10°S	P15S ^a	CGC90	−0.003	0.001	ND ^b	ND ^b	4.2	−2.1 ^c	4.9	−1.1±0.9	3.0±2.5			
7 / 8	170°W	10°S	P15S ^a	EQS92	0.002	0.003	−3.2	1.3	1.5	−1.6	2.5	−1.1±0.9	−0.8±1.2			
7 / 9	170°W	10°S	P15S ^a	P15N	0.001	0.001	−3.0	0.2	2.1	1.1 ^c	0.9	−1.1±0.9	−0.1±2.7			
7 / 10	170°W	10°S	P15S ^a	P31	0.000	0.002	0.0	2.6	−0.8	−0.7	3.2	−1.1±0.9	−0.9±2.7			
8 / 11	170°W	5°S	P15S ^a	P15N	0.001	0.001	−3.3	0.8	7.9	6.9	1.9	−1.1±0.9	−0.1±2.7			
8 / 12	170°W	5°S	P15S ^a	CGC90	−0.002	0.002	ND ^b	ND ^b	6.1	4.2	2.3	−1.1±0.9	3.0±2.5			
8 / 13	170°W	5°S	P15S ^a	EQS92	−0.002	0.002	2.3	5.2	4.7	−2.7	2.8	−1.1±0.9	−0.8±1.2			
9 / 14	170°W	0E	P15S ^a	P15N	−0.001	0.001	−1.3	0.9	1.9	0.9	1.1	−1.1±0.9	−0.1±2.7			
9 / 15	170°W	0E	P15S ^a	CGC90	−0.001	0.000	ND ^b	ND ^b	2.4	1.3	2.4	−1.1±0.9	3.0±2.5			
9 / 16	170°W	0E	P15S ^a	EQS92	0.002	0.001	ND ^b	ND ^b	0.6	0.3	0.4	−1.1±0.9	−0.8±1.2			
10 / 17	152°W	53°N	CGC91	P17	0.000	0.000	ND ^b	ND ^b	−15.1	−12.1 ^d	1.2	3.0±2.5	N/A ^d			
11 / 18	150°W	37°S	P16	P16	−0.001	0.002	1.5	2.5	0.1	0.1	1.6	1.3±1.5	1.3±1.5			
12 / 19	150°W	32°S	P6	P16	0.000	0.001	1.8	0.3	0.4	−1.9	0.4	0.6±1	1.4±2			
13 / 20	150°W	17°S	P16	P21	−0.001	0.000	0.1	0.2	ND ^b	−3.2 ^c	1	±2.0 ^c	0.9±1.1			
13 / 21	150°W	17°S	P21	P31	0.000	0.000	0.3	0.4	3.1	3.1	0.8	0.9±1.1	−0.9±2.7			
13 / 22	150°W	17°S	P31	P16	0.001	0.001	0.4	0.3	ND ^b	0.1	0.6	−0.9±2.7	0.9±1.1			
14 / 23	135°W	53°S	P17	P17	−0.001	0.004	2.3	0.7	−4.5	−4.6	2.9	1.3±1.5	1.4±2.1			
15 / 24	135°W	33°S	P6	P17	−0.001	0.001	0.0	1.2	−3.5	−1.2	0.5	0.6±1.9	1.4±2.1			
16 / 25	135°W	17°S	P17	P21	0.000	0.000	1.2	1.1	3	−0.7	2.9	1.4±2.1	0.9±1.1			
17 / 26	135°W	5°S	P17	P17	0.000	0.001	−0.2	2.1	0.9	−0.5	2.9	1.3±1.5	N/A ^d			
18 / 27	135°W	35°N	P17	P17	−0.003	0.001	3.4	0.9	ND ^b	−0.8	8.0	N/A ^d	N/A ^d			
19 / 28	135°W	40°N	CGC91	P17	−0.007	0.019	11.5	11.9	−1.7	1.3	2.1	3.0±2.5	N/A ^d			
20 / 29	126°W	67°S	S4	P17	0.011	0.019	−6.1	7.1	2.1	−0.4	1.9	−0.9±1.8	1.4±2.1			
21 / 30	110°W	0E	P18	EQS92	−0.012	0.012	0.6	6.0	0	−1.5 ^e	3.7	−1.3±1.4	−0.8±1.2			
21 / 31	110°W	0E	P18	EQF92	0.018	0.022	−3.2	1.6	−1.4 ^e	−1.3 ^e	2.3	−1.3±1.4	−0.9±1.2			
22 / 32	110°W	5°N	P18	EQS92	−0.006	0.004	−5.1 ^e	1.5	1.8	−0.5	6.3	−1.3±1.4	−0.8±1.2			
22 / 33	110°W	5°N	P18	EQF92	−0.001	0.004	3.7	6.6	−5.4	−6.3	7.2	−1.3±1.4	−0.9±1.2			
23 / 34	103°W	67°S	P18	S4	0.002	0.002	−5.1	3.9	−0.4 ^f	1.4 ^f	1.0	−1.3±1.4	−0.9±1.8			

24 / 35	103°W	32°S	P18	P6	0.001	0.002	0.6	1.5	-0.1	0.0	1.3	-1.3±1.4	0.6±1.9
25 / 36	103°W	17°S	P18	P21	0.001	0.002	-1.4	0.6	1.9 ^g	0.5	1.2	-1.3±1.4	0.1±2.7
26 / 37	88°W	67°S	S4	P19	-0.005	0.001	3.5	0.2	0.2	-1.4 ^e	0.6	-0.9±1.8	$\frac{-0.2 \pm 1.9}{9}$
27 / 38	88°W	32°S	P19	P6	0.003	0.004	-2.5	3.0	0.2	0.9	1.3	-0.2±1.9	0.6±1.9
28 / 39	86°W	55°S	P19	P19	-0.001	0.001	0.4	0.2	0.9	-0.7	0.5	-0.2±1.9	1.4±2.1
29 / 40	86°W	17°S	P19	P21	0.000	0.001	0.3	0.9	-1.6	-2.7	0.3	-0.2±1.9	0.9±1.1
30 / 41	86°W	13°S	P19	EQF92	0.012	0.008	0.1	3.8	-0.2	-0.4	4.8	-0.2±1.9	$\frac{-0.9 \pm 1.9}{2}$
Mean of the absolute value of the difference					0.003		2.3		2.4	1.9			
SD of the absolute value of the difference					0.004		2.4		2.8	2.3			

^aPreliminary data.

^bND = no data.

^cCRMs used as primary standard.

^dCRMs not available.

^eLinear regression applied.

^fAverage of two separate fits.

^g4th order polynomial.

Table 4. Summary of the comparison results for the fugacity of CO₂(*f*CO₂) for each of the 16 crossover comparisons during the Global CO₂ Survey in the Pacific

Location number/ Crossover comparison	Nominal position		Cruise name/ WOCE line) Salinity between cruises	SD Salinity between cruises) O ₂ between cruises	SD O ₂ between cruises (Fmol/kg)) <i>f</i> CO ₂ between cruises (Fatm)	SD <i>f</i> CO ₂ between cruises (Fatm)
	Long.	Lat.	Cruise 1	Cruise 2						
1 / 1	170° E	66° S	*P14S ^a	†S4	0.003	0.002	−1.0	0.2	3.8	2.6
4 / 4	170° W	67° S	*P15S ^a	†S4	0.005	0.002	−1.6	0.2	2.8	1
7 / 8	170° W	10° S	*P15S ^a	*EQS9 2	0.002	0.003	−3.2	1.3	30.3	8.9
8 / 13	170° W	5° S	*P15S ^a	*EQS9 2	−0.002	0.002	2.3	5.2	17.2	25.8
9 / 16	170° W	0E	*P15S ^a	*EQS9 2	0.002	0.001	ND ^b	ND ^b	13.9	12.0
11 / 18	150° W	37° S	*P16	*P16	−0.001	0.002	1.5	2.5	3.2	10.4
14 / 23	135° W	53° S	†P17	†P17	−0.001	0.004	2.3	0.7	4.7	8.8
20 / 29	126° W	67° S	†S4	†P17	0.011	0.019	−6.1	7.1	9.8 ^c	8.2
21 / 30	110° W	0E	*P18	*EQS9 2	−0.012	0.012	0.6	6.0	−28.7 ^c	41.5
21 / 31	110° W	0E	*P18	*EQF9 2	0.018	0.022	−3.2	1.6	−12.9	25.1
22 / 32	110° W	5° N	*P18	*EQS9 2	−0.006	0.004	−5.1 ^c	1.5	67.1	10.9
22 / 33	110° W	5° N	*P18	*EQF9 2	−0.001	0.004	3.7	6.6	34.0 ^c	74.1
23 / 34	103° W	67° S	*P18	†S4	0.002	0.002	−5.1	3.9	−8.0	5.5
26 / 37	88° W	67° S	†S4	†P19	−0.005	0.001	3.5	0.2	−13.1	1.9
28 / 39	86° W	55° S	†P19	†P19	−0.001	0.001	0.4	0.2	14.2	4.3
30 / 41	86° W	13° S	*P19	*EQF9 2	0.012	0.008	0.1	3.8	18.8	47.2
Mean of the absolute value of the difference									17.6	
Standard deviation of the absolute value of the difference									16.3	

^aPreliminary data.

^bND = no data.

^cLinear regression applied.

*Measured at 20°C.

†Measured at 4°C.

Table 5. Summary of the comparison results for total alkalinity (TAlk) for each of the 15 crossover comparisons during the Global CO₂ Survey in the Pacific

Location number/ Crossover comparison	Nominal position		Cruise name/ WOCE line) Salinity between cruises	SD Salinity between cruises) O ₂ between cruises (Fmol/kg)	SD O ₂ between cruises (Fmol/kg)) TAlk between cruises (Fmol/kg)	SD TAlk between cruises (Fmol/kg)
	Long.	Lat.	Cruise 1	Cruise 2	Cruise 1–2		Cruise 1–2		Cruise 1–2	
6 / 6	170°W	17°S	P15S	P21	–0.007	0.001	–6.0	1.7	–0.2	0.3
7 / 9	170°W	10°S	P15S	P15N	0.001	0.001	–3.0	0.2	–5.4	10.4
7 / 10	170°W	10°S	P15S	P31	0.000	0.002	0.0	2.6	3.5	5.6
8 / 11	170°W	5°S	P15S	P15N	0.001	0.001	–3.3	0.8	4.6	2.1
8 / 13	170°W	5°S	P15S	EQS92	–0.002	0.002	2.3	5.2	7.3	8.3
9 / 14	170°W	0°E	P15S	P15N	–0.001	0.001	–1.3	0.9	7.1	1.1
9 / 16	170°W	0°E	P15S	EQS92	0.002	0.001	2.2	1.2	3.5	5.4
13 / 20	150°W	17°S	P16	P21	–0.003	0.005	0.1	0.2	1	0.9
13 / 21	150°W	17°S	P21	P31	0.001	0.005	0.3	0.4	–7.3	1.1
13 / 22	150°W	17°S	P31	P16	0.002	0.002	0.4	0.3	6.3	2
21 / 30	110°W	0°E	P18	EQS92	–0.012	0.012	0.6	6.0	–10.9	6.6
21 / 31	110°W	0°E	P18	EQF92	0.018	0.022	–3.2	1.6	–7.5	7.7
22 / 32	110°W	5°N	P18	EQS92	–0.006	0.004	–5.1 ^b	1.5	–11.5	4.6
22 / 33	110°W	5°N	P18	EQF92	–0.001	0.004	3.7	6.6	7.8	4
25 / 36	103°W	17°S	P18	P21	0.004	0.004	–0.9	1.5	–2.1	0.8
Mean of the absolute value of the difference									5.7	
Standard deviation of the absolute value of the difference									3.3	

^aND = no data.

^bLinear regression applied.

Table 6. Summary of the comparison results for pH for each of the 5 crossover comparisons during the Global CO₂ Survey in the Pacific

Location number/ Crossover comparison	Nominal position		Cruise name/ WOCE line) Salinity between cruises	SD Salinity between cruises) O ₂ between cruises (Fmol/kg)	SD O ₂ between cruises (Fmol/kg)) pH between cruises	SD pH between cruises
	Long.	Lat.	Cruise	Cruise 2	Cruise 1–2		Cruise 1–2		Cruise 1–2	
6 / 6	170° W	17°S	P15S	P21	0.007	0.001	–6.0	1.7	0.0062	0
7 / 8	170° W	10°S	P15S	EQS92	0.002	0.003	–3.2	1.3	0.0006	0
7 / 10	170° W	10°S	P15S	P31	0.000	0.002	0.0	2.6	–0.0005	0.0003
8 / 13	170° W	5°S	P15S	EQS92	–0.002	0.002	2.3	5.2	0.0035	0.011
9 / 16	170° W	0	P15S	EQS92	0.002	0.001	ND ^a	ND ^a	0.0008	0
Mean of the absolute value of the difference									0.0023	
Standard deviation of the absolute value of the difference									0.0025	

^aND = no data.

Table 7. The effect of constants on the calculation of the fugacity of CO₂ (f_{CO_2}) at 20°C^a

Source of constants	Input	Input	Input	Input	Output	Output	Output
	DIC	Si(OH) ₄	PO ₄	f_{CO_2} @4°C	Talk	f_{CO_2} @20°C	γ_{CO_2} @20°C/ γ_{DIC}
Roy et al. (1993)	2260	135	2.3	531.8	2371.3	1080	7.1
Goyet and Poisson (1989)	2260	135	2.3	531.8	2371.3	1076.4	7.1
Hansson (1973a,b) refit by Dickson and Millero (1987)	2260	135	2.3	531.8	2377.4	1018.8	6.7
Mehrbach et al. (1973) refit by Dickson and Millero (1987)	2260	135	2.3	531.8	2368.4	1033.0	7
Dickson and Millero (1987) refit of Hansson/Mehrbach	2260	135	2.3	531.8	2372.5	1042.7	6.9
GEOSECS (Takahashi et al. 1982)	2260	135	2.3	531.8	2367.2	1016.8	6.9
Peng et al. (1987)	2260	135	2.3	531.8	2378.1	1013.3	6.7

^aAll values were calculated using the QUICKBASIC computer program of Lewis and Wallace (1998) with the default values for the secondary constants; the correction from 4°C to 20°C can cause the resulting pCO₂ to differ by 65 Fatm depending on the constants used. The γ_{CO_2} @20°C/ γ_{DIC} values in Fatm/(Fmol/kg) show that in Pacific deep water a precision of 1.5 Fmol/kg in DIC corresponds to approximately 10 Fatm in f_{CO_2} .

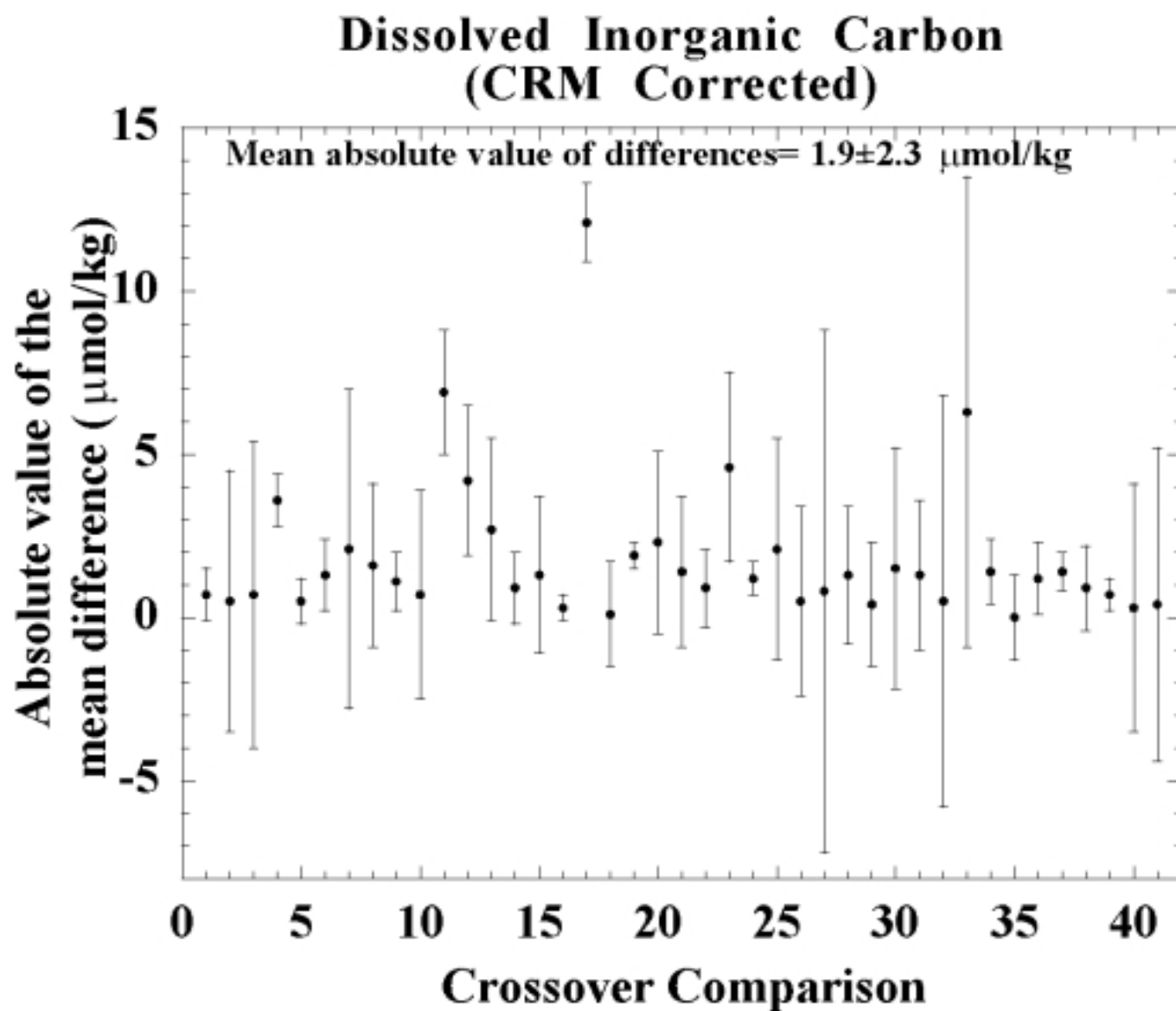


Fig. 2. Absolute value of the mean difference of DIC (CRM corrected) for the 41 crossover comparisons.

Location #/ Crossover Comparison	Nominal Position	
	Long.	Lat.
1 / 1	170°E	66°S
2 / 2	178°W	32°S
3 / 3	175°W	32°S
4 / 4	170°W	67°S
5 / 5	170°W	32°S
6 / 6	170°W	17°S
7 / 7	170°W	10°S
7 / 8	170°W	10°S
7 / 9	170°W	10°S
7 / 10	170°W	10°S
8 / 11	170°W	5°S
8 / 12	170°W	5°S
8 / 13	170°W	5°S
9 / 14	170°W	0
9 / 15	170°W	0
9 / 16	170°W	0
10 / 17	152°W	53°N
11 / 18	150°W	37°S
12 / 19	150°W	32°S
13 / 20	150°W	17°S
13 / 21	150°W	17°S
13 / 22	150°W	17°S
14 / 23	135°W	53°S
15 / 24	135°W	33°S
16 / 25	135°W	17°S
17 / 26	135°W	6°S
18 / 27	135°W	35°N
19 / 28	135°W	40°N
20 / 29	126°W	67°S
21 / 30	110°W	0
21 / 31	110°W	0
22 / 32	110°W	5°N
22 / 33	110°W	5°N
23 / 34	103°W	67°S
24 / 35	103°W	32°S
25 / 36	103°W	17°S
26 / 37	88°W	67°S
27 / 38	88°W	32°S
28 / 39	86°W	55°S
29 / 40	86°W	17°S
30 / 41	86°W	13°S

The agreement of the TAlk data between the 15 crossover locations is not quite as good as the DIC results. The differences between cruises ranged from -11.5 to 7.8 Fmol/kg; generally, the smallest differences correspond to the excellent agreement by the same laboratory on different cruises. As with DIC and $f\text{CO}_2$, the largest offsets generally occur during the strong El Nino event in 1992. The mean of the absolute value of the difference was 5.7 ± 3.3 Fmol/kg; this corresponds to a mean uncertainty of approximately 0.2%. CRMs were available for TAlk where crossover comparisons were made for this report, and all data have been normalized to the certified values.

Three laboratories performed pH analyses, and as a result, only five crossover locations were available to compare the pH results. All comparisons were made on the total seawater scale. The differences ranged from -0.0005 to 0.0062 and the mean of the absolute value of the difference was 0.0023 ± 0.0025 . In the deep Pacific, an uncertainty of 1 Fmol/kg DIC is equivalent to approximately 0.003 pH units. These results suggest that the limited amount of pH data in the Pacific were in excellent agreement with each other.

The summary data in Tables 3–6 should be viewed as one of several indicators of the overall quality of the carbon data from the Pacific. In addition to these results, there also are the shore-based analyses of replicate DIC samples taken during each of the cruises (Guenther et al. 1994) and the interlaboratory analyses of the CRMs (Dickson 1992). These three pieces of information should be used together with thermodynamic models in the process of evaluating the overall quality of the database. In several cases, particularly with respect to the NOAA data sets, three or four carbon parameters were measured during the cruises. In these situations, the internal consistency of the individual parameters in the data sets can be checked using an appropriate thermodynamic model (Millero et al. 1993; Byrne et al., in press; Wanninkhof et al., 1999). In this way, two parameters may be used to check the validity of the third and, in some cases, fourth parameter. For example, very precise and accurate DIC and pH data may be used to validate the $f\text{CO}_2$ and TAlk data. We recommend that individual data sets be evaluated in this manner before they are used in physical and biogeochemical models. In addition, it is our recommendation that DIC data are reported to the database manager as both uncorrected and corrected with respect to CRMs, and that the CRM results are appended in a “meta” file. This file should contain at minimum CRM batch number, number of CRMs run, the given value and observed values, along with the standard deviation and number of CRM results rejected. The method of correction of the data should be clearly described, including if the correction was applied per cell, per cruise, using a longer-term mean, or if the correction was an additive or a ratio. In order to obtain a coherent data set of DIC from this program, it is imperative that the data be corrected in the same way. As shown in this report, the crossover data for DIC are statistically improved when the correction is applied. We also recommend the TAlk data be reported to the database manager in a similar way, appending a “meta” file containing a description of the CRM results. In addition, it is useful for both CRM corrected and uncorrected TAlk data to be submitted.

4. CONCLUSIONS

The comparison of the carbon system parameters during the WOCE and OACES cruises in the North and South Pacific has provided unique information on data quality at the crossover locations. For DIC, $f\text{CO}_2$, and pH, the agreement at most crossover locations is well within the design specifications for the global CO_2 survey, despite the lack of CRMs for both $f\text{CO}_2$ and pH. In a statistical analysis performed on DIC data that were corrected to CRM values vs noncorrected values, results indicate there is a significant difference between the two. On the other hand, although normalized to CRM values for TALK, the comparisons made in this report for that parameter were not as good. The outcome of this comparison stresses the importance of CRMs, as well as the value of building some redundant measurements into the program to provide an independent check on data quality.

Since the inception of this document, we have made every attempt to include the most up-to-date information available; however, large data sets are constantly evolving. Some of the data presented in this report are expected to change as the data are further evaluated. To access the latest data sets, please check the web sites listed in Section 5.

5. REMOTE ACCESS TO DATA LISTED IN THIS REPORT

Much of the data presented in this report are available on the World Wide Web (WWW). For information regarding electronic access to the data sets contact:

For NOAA/OACES data:

NOAA/AOML/OCD	Telephone: (305)361-4399 (voice)
4301 Rickenbacker Causeway	(305)361-4392 (fax)
Miami, Florida 33149-1026	
U.S.A.	
Internet: http://www.aoml.noaa.gov/ocd/oaces	

For DOE Global CO_2 survey data:

Carbon Dioxide Information Analysis Center	Telephone:(865)574-3645 (voice)
Oak Ridge National Laboratory	(865)574-2232 (fax)
P.O. Box 2008	
Oak Ridge, Tennessee 37831-6335	
U.S.A.	
Internet: http://cdiac.esd.ornl.gov/oceans/home.html	

Graphics of the data contained in this report are also available at http://www.pmel.noaa.gov/co2/oaces_doe/home.html.

6. ACKNOWLEDGMENTS

This research was supported by the NOAA Climate and Global Change Program as part of the joint NOAA/DOE/NSF cosponsored carbon component of the Ocean-Atmosphere Carbon Exchange Study and the World Ocean Circulation Experiment. It is also a component of the U.S. JGOFS Synthesis and Modeling Project and NOAA Global Carbon Cycle Program. We thank Drs. Lisa Dilling and James F. Todd of the NOAA Office of Global Programs; Drs. John Downing, Curtis Olson, and Mike Riches of the Department of Energy; and Dr. Donald Rice of the National Science Foundation for program coordination and support. We also thank all the scientists and technicians involved with the Pacific expeditions. Their excellent spirit of cooperation played a significant role in obtaining the high-quality data used in this report.

7. REFERENCES

- Byrne, R. H., S. McElligott, R. A. Feely, and F. J. Millero. The role of pH_T measurements in CO_2 system characterizations. *Deep-Sea Res.* (in press).
- Dickson, A. G. 1992. The determination of total dissolved inorganic carbon in sea water using extraction/coulometry: The first stage of a collaborative study. DOE/RL/01830T-H14. U.S. Department of Energy.
- Dickson, A. G., J. D. Afghan, and G. C. Anderson. Sea water based reference materials for CO_2 analysis: 2. A method for the certification of total alkalinity. *Mar. Chem.* (unpublished manuscript).
- Dickson, A. G., G. C. Anderson, and J. D. Afghan. Sea water based reference materials for CO_2 analysis: 1. Preparation, distribution and use. *Mar. Chem.* (unpublished manuscript).
- Dickson, A. G., and F. J. Millero. 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Res.* 34:1733–43.
- Dickson, A. G., and F. J. Millero. 1989. Corrigenda. *Deep-Sea Res.* 36:983.
- DOE (U.S. Department of Energy). 1994. *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water. Version 2.* ORNL/CDIAC-74. A. G. Dickson and C. Goyet (eds.), Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tenn.
- Feely, R. A., R. Wanninkhof, C. E. Cosca, P. P. Murphy, M. F. Lamb, and M. D. Steckley. 1995. CO_2 distributions in the equatorial Pacific during the 1991–1992 ENSO event. *Deep-Sea Res. Part II* 42(2–3):365–86.
- Gordon, L. I., C. Mordy, J. Wilson, and A. A. Ross. 1998. A study of discrepancies in observed nutrient concentrations at WHP Pacific line intersections: An accuracy estimate. pp. 24–29. In *Ocean Circulation and Climate*, Proceedings of the 1998 Conference of the World Ocean Circulation Experiment (WOCE), May 24–29, 1998, Halifax, Nova Scotia, Canada.
- Goyet, C., and A. Poisson. 1989. New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity. *Deep-Sea Res.* 36:1635–1654.
- Guenther, P. R., C. D. Keeling, and G. Emanuele III. 1994. Oceanic CO_2 measurements for the WOCE Hydrographic Survey in the Pacific Ocean, 1990–1991: Shore based analyses. Scripps Institution of Oceanography Reference Series, Ref. No. 94-28. University of California, San Diego, Calif.
- Hansson, I. 1973a. A new set of acidity constants for carbonic acid and boric acid in sea water. *Deep-Sea Res.* 20:461–78.

- Hansson, I. 1973b. The determination of dissociation constants of carbonic acid in synthetic sea water in the salinity range of 20–40‰ and temperature range of 5–30°C. *Acta Chemica Scandinavica* 27:931–44.
- Johnson, K. M. 1992. *Operator's Manual: Single Operator Multiparameter Metabolic Analyzer (Somma) for Total Carbon Dioxide (C_T) with Coulometric Detection*. Brookhaven National Laboratory, Upton, N.Y.
- Johnson, K. M., A. G. Dickson, G. Eiseid, C. Goyet, P. Guenther, R. M. Key, F. J. Millero, D. Purkerson, C. L. Sabine, R. G. Schottle, D. R. W. Wallace, R. J. Wilke, and C. D. Winn. 1998. Coulometric total carbon dioxide analysis for marine studies: Assessment of the quality of total inorganic carbon measurements during the WOCE Indian Ocean CO₂ Survey 1994–1996. *Mar. Chem.* 63:21–37.
- Johnson, K. M., A. E. King, and J. McN. Sieburth. 1985. Coulometric TCO₂ analyses for marine studies: An introduction. *Mar. Chem.* 16:61–82.
- Johnson, K. M., P. J. Williams, L. Brandstrom, and J. McN. Sieburth. 1987. Coulometric total carbon analysis for marine studies: Automation and calibration. *Mar. Chem.* 21:117–33.
- Johnson, K. M., K. D. Wills, D. B. Butler, W. K. Johnson, and C. S. Wong. 1993. Coulometric total carbon dioxide analysis for marine studies: Maximizing the performance of an automated continuous gas extraction system and coulometric detector. *Mar. Chem.* 44:167–89.
- Lewis, E. R., and D. W. R. Wallace. 1998. Program developed for CO₂ system calculations. ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U. S. Department of Energy, Oak Ridge, Tenn.
- Merzbach, C., C. H. Culberson, J. E. Hawley, and R. M. Pytkowicz. 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr.* 18:897–907.
- Millero, F. J., R. H. Byrne, R. Wanninkhof, R. A. Feely, T. Clayton, P. P. Murphy, and M. F. Lamb. 1993. The internal consistency of CO₂ measurements in the equatorial Pacific. *Mar. Chem.* 44:269–80.
- Millero, F. J., A. G. Dickson, G. Eiseid, C. Goyet, P. Guenther, K. M. Johnson, R. M. Key, K. Lee, D. Purkerson, C. L. Sabine, R. G. Schottle, D. R. W. Wallace, E. Lewis, and C. D. Winn. 1998. Assessment of the quality of the shipboard measurements of total alkalinity on the WOCE Hydrographic Indian Ocean CO₂ survey cruises 1994–1996. *Mar. Chem.* 63:9–20.
- Peng, T. H., T. Takahashi, W. S. Broecker, and J. Olafsson. 1987. Seasonal variability of carbon dioxide, nutrients and oxygen in the northern North Atlantic surface water: Observations and model. *Tellus* 39B:439–58.
- Roy, R. N., L. N. Roy, K. M. Vogel, C. Porter-Moore, T. Pearson, C. E. Good, F. J. Millero, and D. M. Campbell. 1993. The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45°C. *Mar. Chem.* 44:249–67.

- Roy, R. N., L. N. Roy, K. M. Vogel, C. Porter-Moore, T. Pearson, C. E. Good, F. J. Millero, and D. M. Campbell. 1994. Erratum. *Mar. Chem.* 45:337.
- Roy, R. N., L. N. Roy, K. M. Vogel, C. Porter-Moore, T. Pearson, C. E. Good, F. J. Millero, and D. M. Campbell. 1996. Erratum. *Mar. Chem.* 52:183.
- Takahashi, T., R. T. Williams, and D. L. Bos. 1982. Carbonate chemistry. pp. 77–83. In W. S. Broecker, D. W. Spencer, and H. Craig. *GEOSECS Pacific Expedition, Volume 3: Hydrographic Data 1973–1974*. National Science Foundation, Washington, D.C.
- UNESCO. 1991. Reference materials for oceanic carbon dioxide measurements. UNESCO Technical Papers in Marine Science No. 60.
- Wanninkhof, R., E. R. Lewis, R. A. Feely, and F. J. Millero. 1999. The optimal carbonate dissociation constants for determining surface water $p\text{CO}_2$ from alkalinity and total inorganic carbon. *Mar. Chem.* 60:15-31.
- WOCE (World Ocean Circulation Experiment). 1994. *WOCE Operations Manual, Volume 3: The Observational Program*, Section 3.1: WOCE Hydrographic Program, Part 3.1.2: Requirements for WHP Data Reporting. (T. Joyce and C. Corry, eds.), WHP Office Report WHPO 90-1 (Revision 2), WOCE Report No. 67/91, Woods Hole, Mass.

APPENDIX A

PLOTS OF THE CROSSOVER COMPARISONS IN THE NORTH AND SOUTH PACIFIC

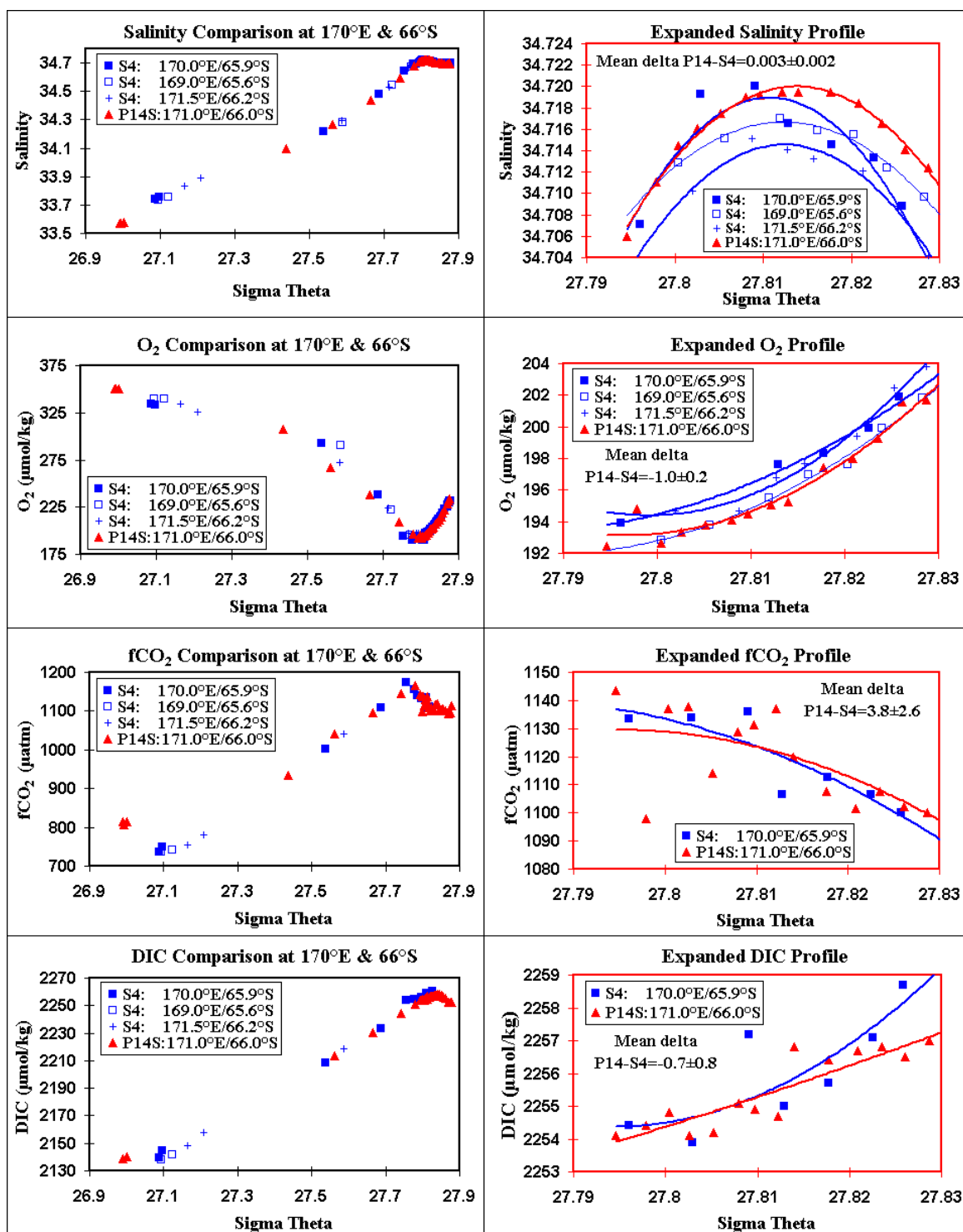


Fig. A.1. Comparison of salinity, oxygen (O₂), fugacity of CO₂ (fCO₂), and dissolved inorganic carbon (DIC) at 170° E and 66° S.

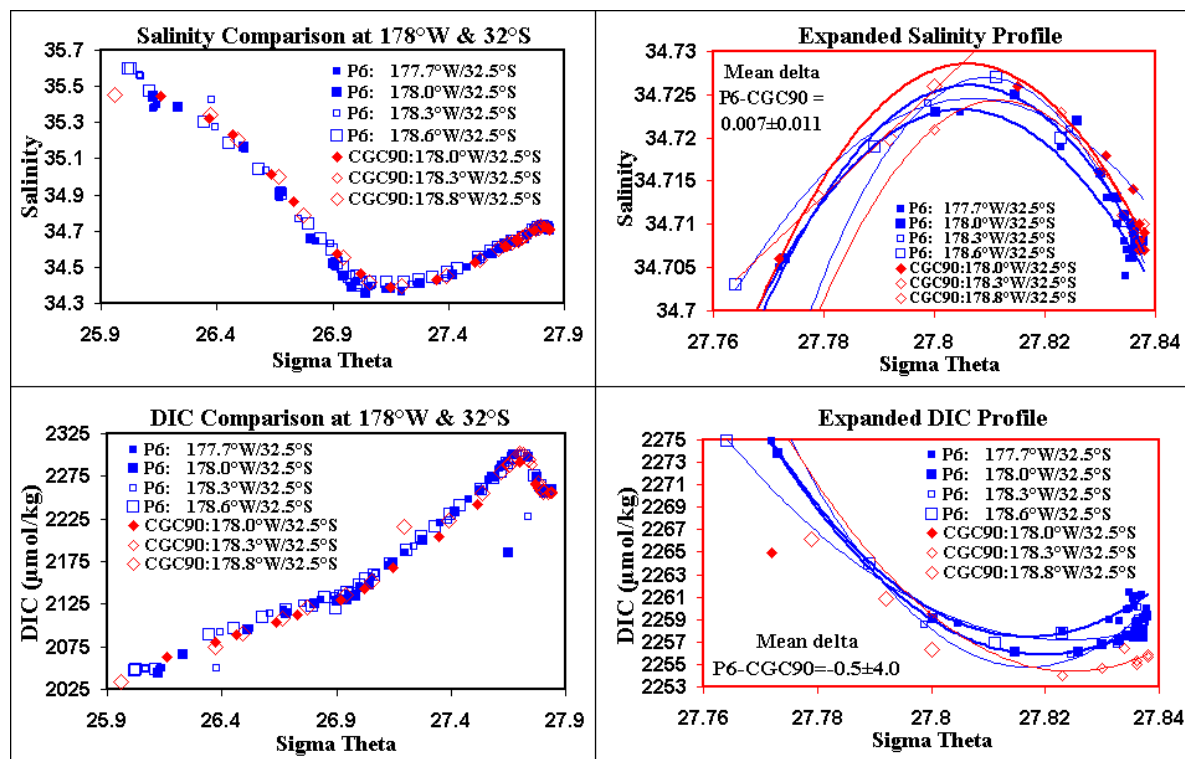


Fig. A.2. Comparison of salinity and dissolved inorganic carbon (DIC) at 178° W and 32° S.

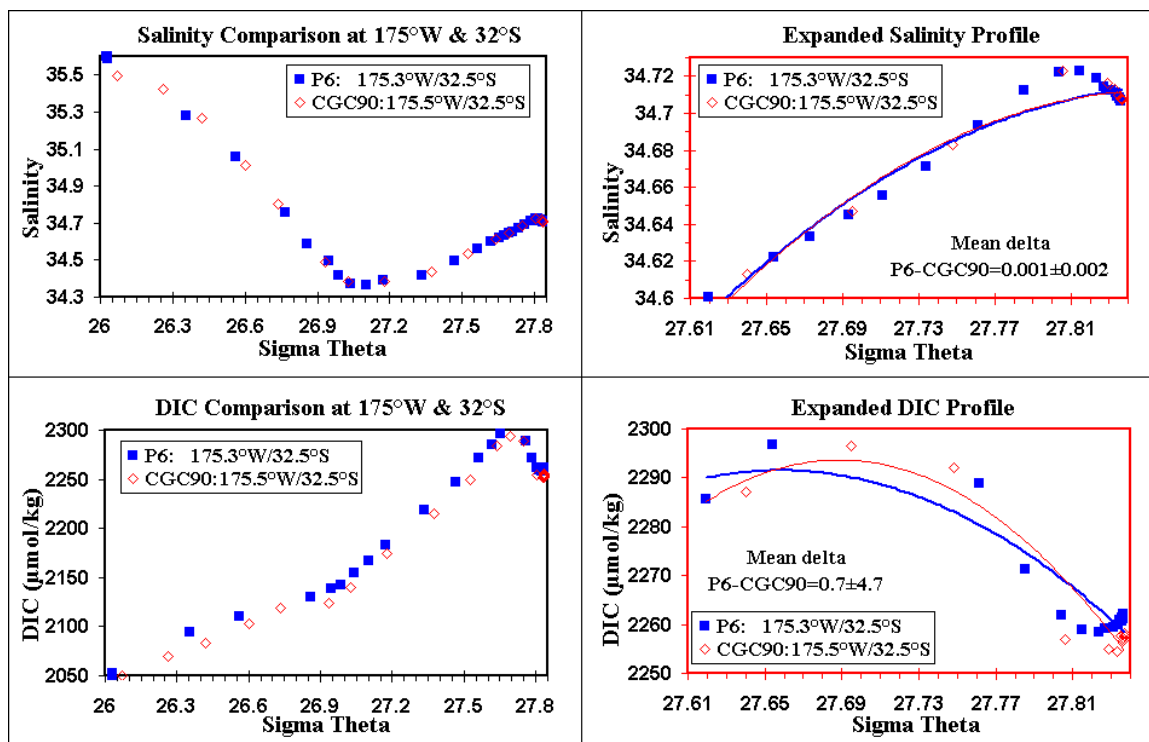


Fig. A.3. Comparison of salinity and dissolved inorganic carbon (DIC) at 175° W and 32° S.

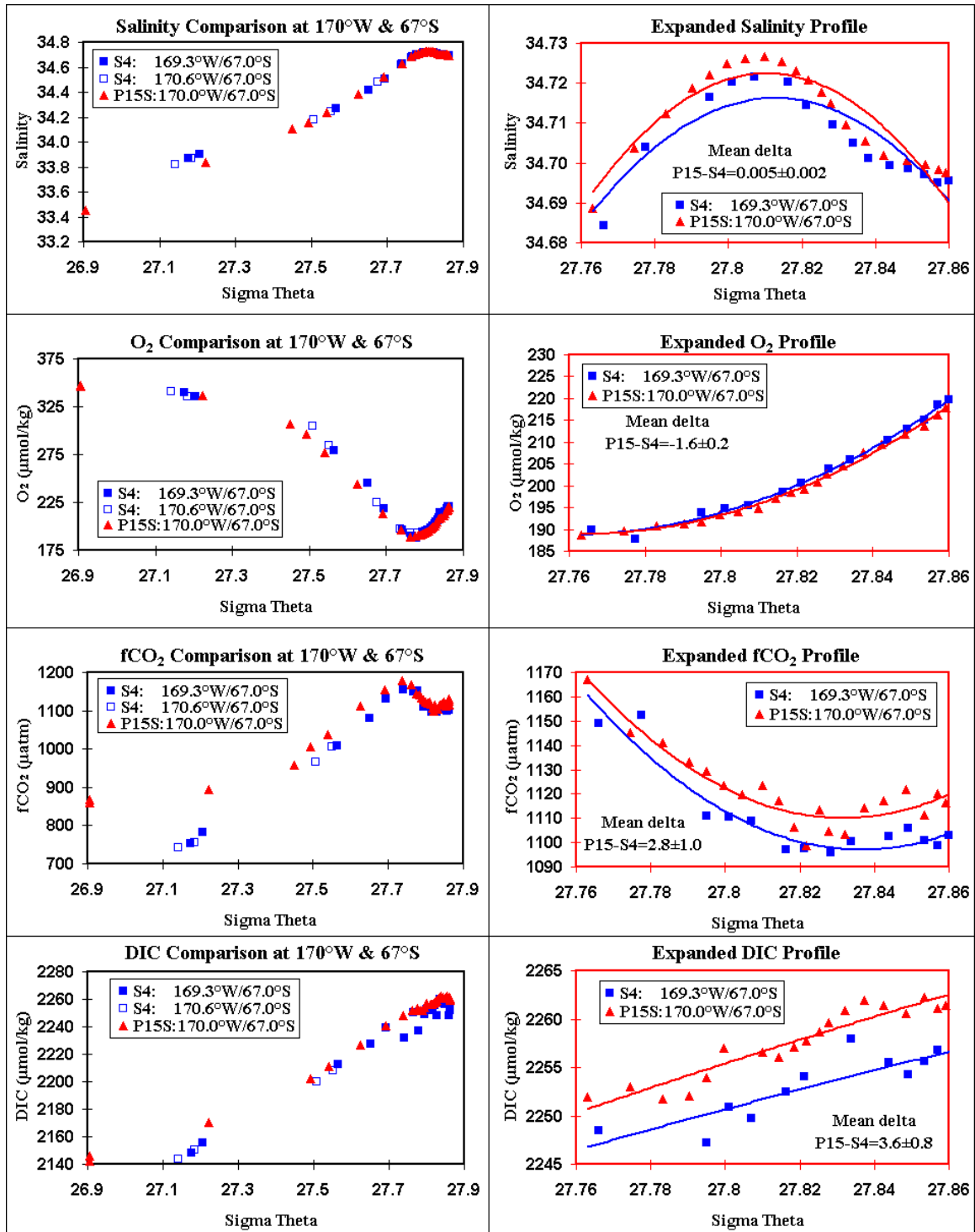


Fig. A.4. Comparison of salinity, oxygen (O₂), fugacity of CO₂ (fCO₂), and dissolved inorganic carbon (DIC) at 170° W and 67° S.

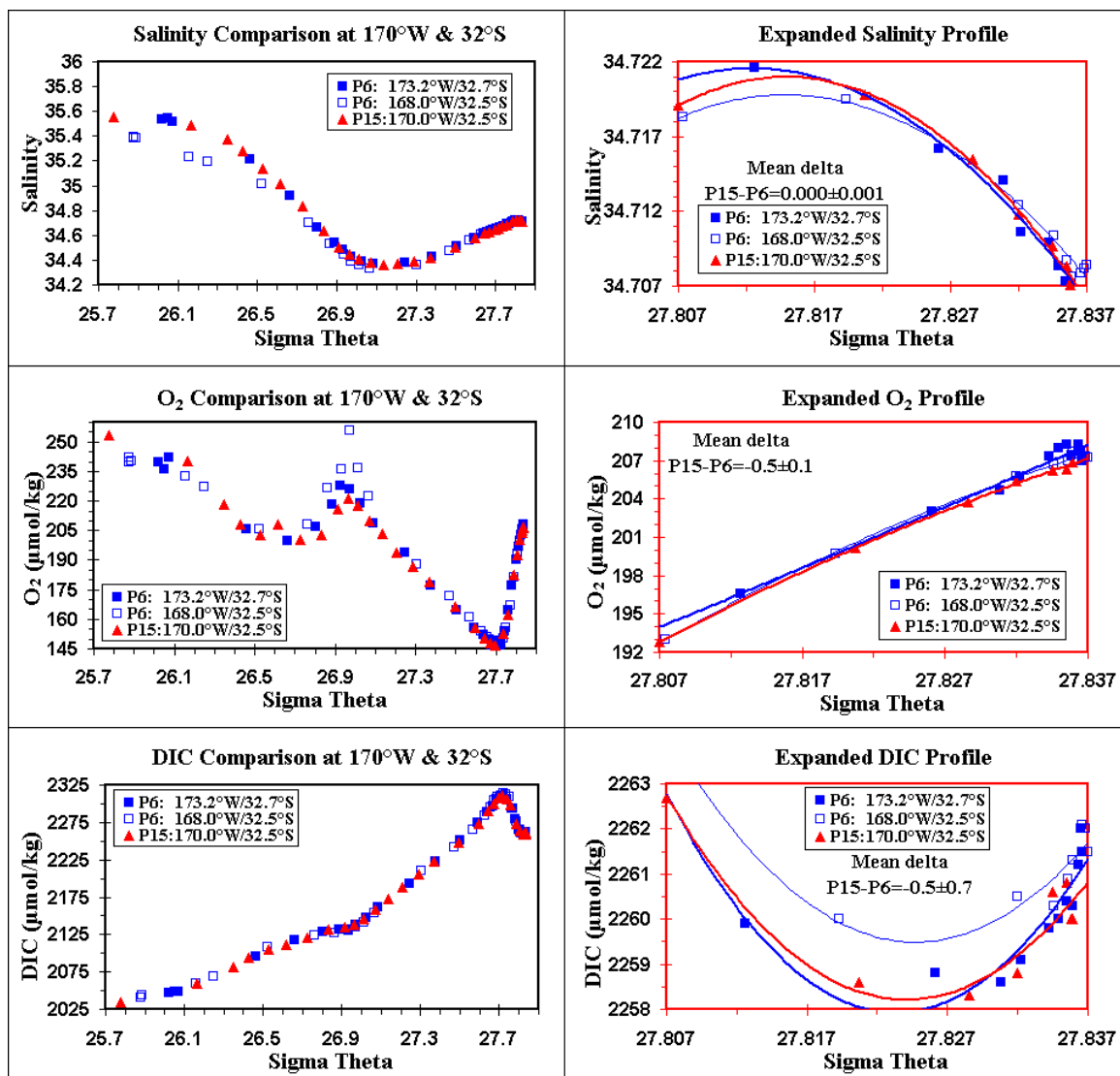


Fig. A.5. Comparison of salinity, oxygen (O₂), and dissolved inorganic carbon (DIC) at 170° W and 32° S.

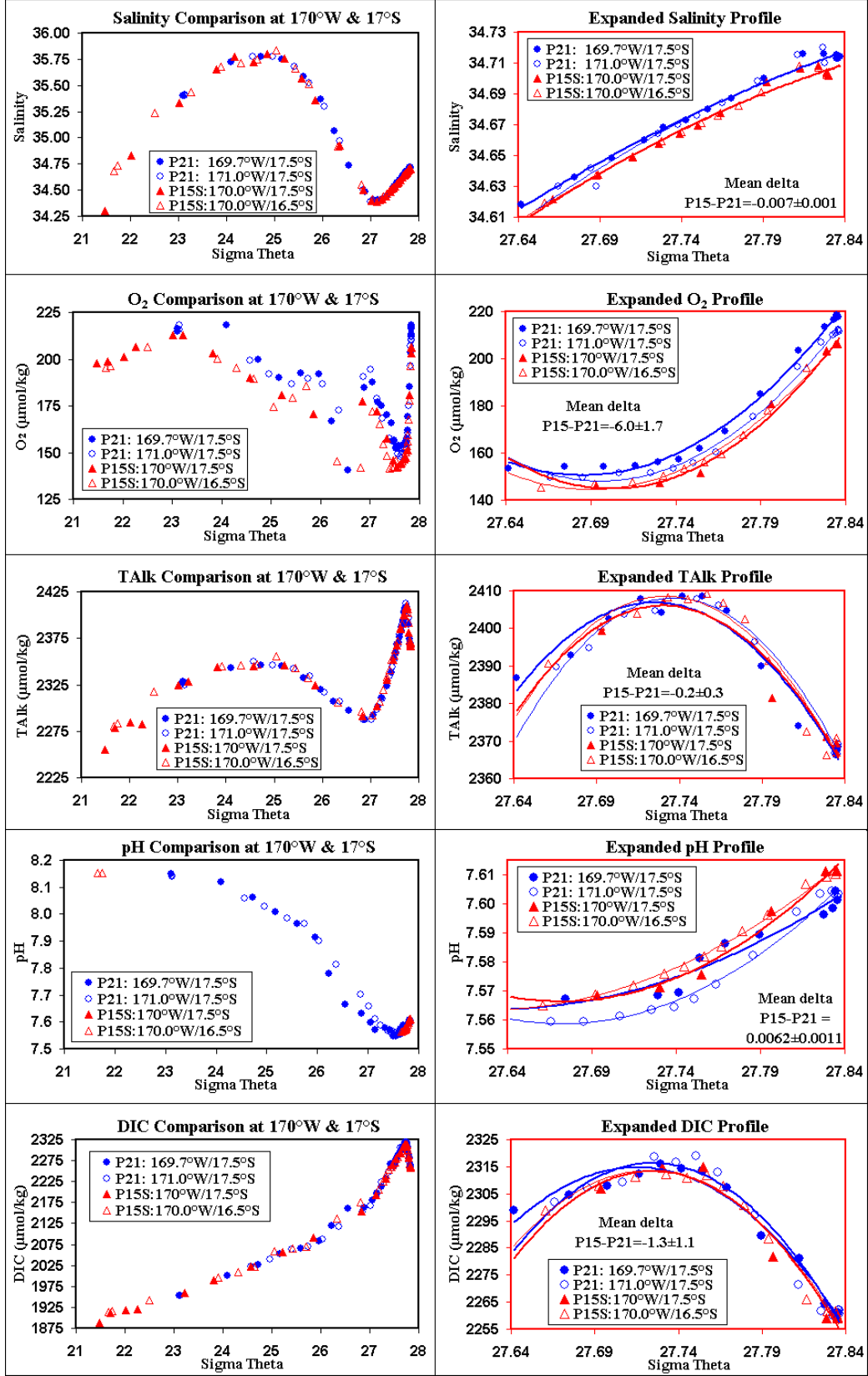


Fig. A.6. Comparison of salinity, oxygen (O₂), total alkalinity (Talk), pH, and dissolved inorganic carbon (DIC) at 170° W and 17° S.

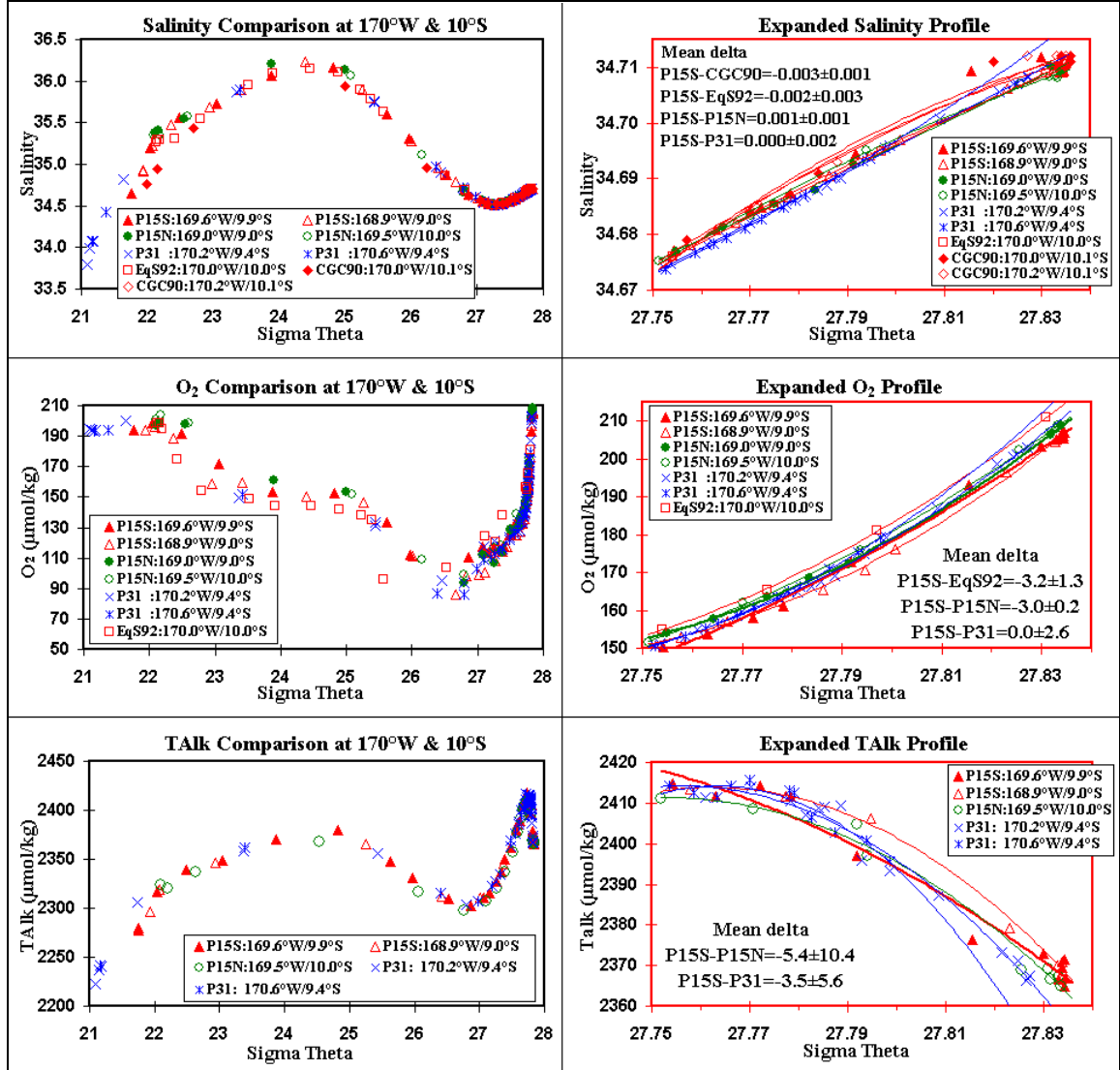


Fig. A.7a. Comparison of salinity, oxygen (O₂), and total alkalinity (TALK) at 170° W and 10° S.

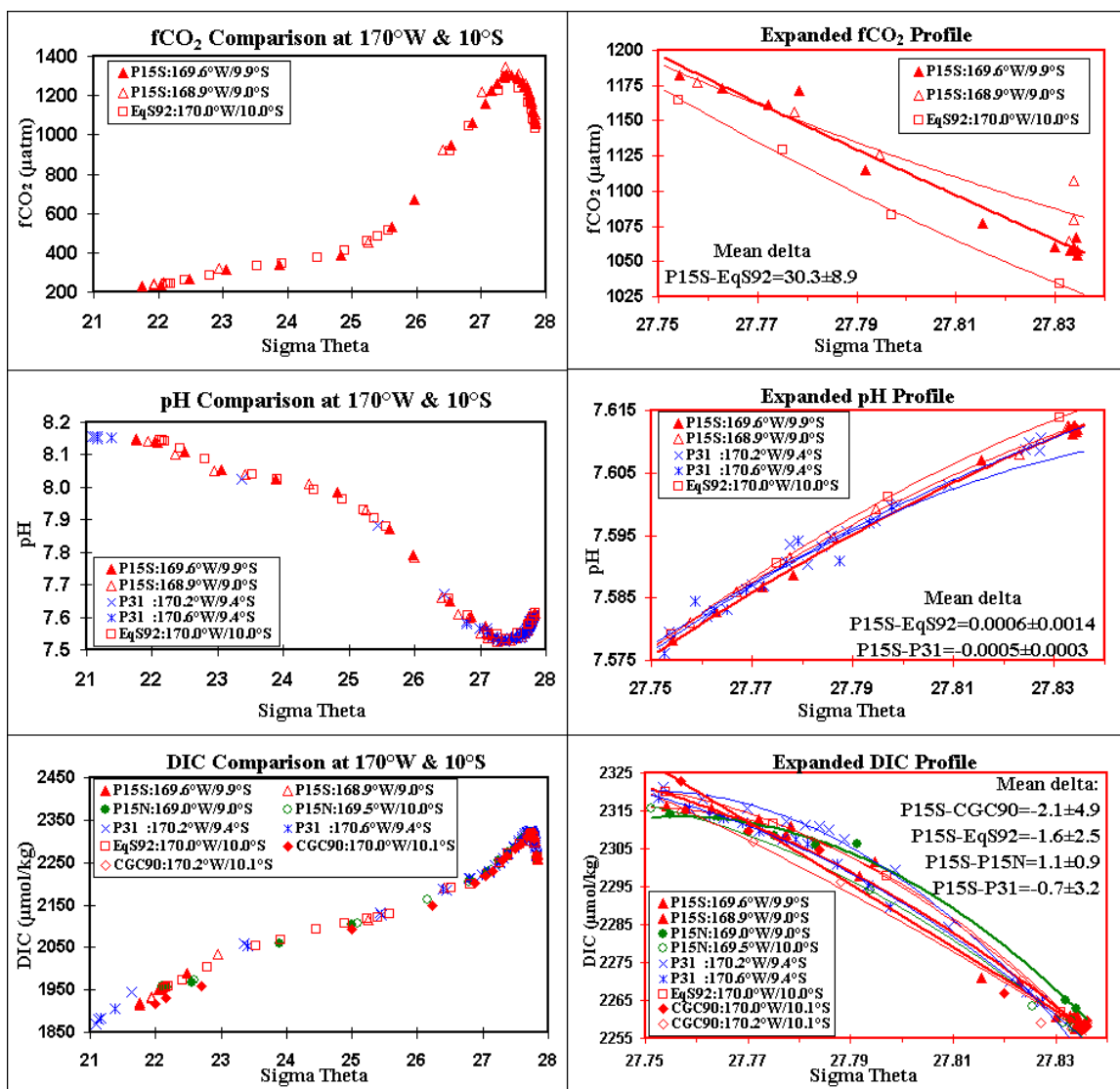


Fig. A.7b. Comparison of fugacity of CO₂ (fCO₂), pH, and dissolved inorganic carbon (DIC) at 170° W and 10° S.

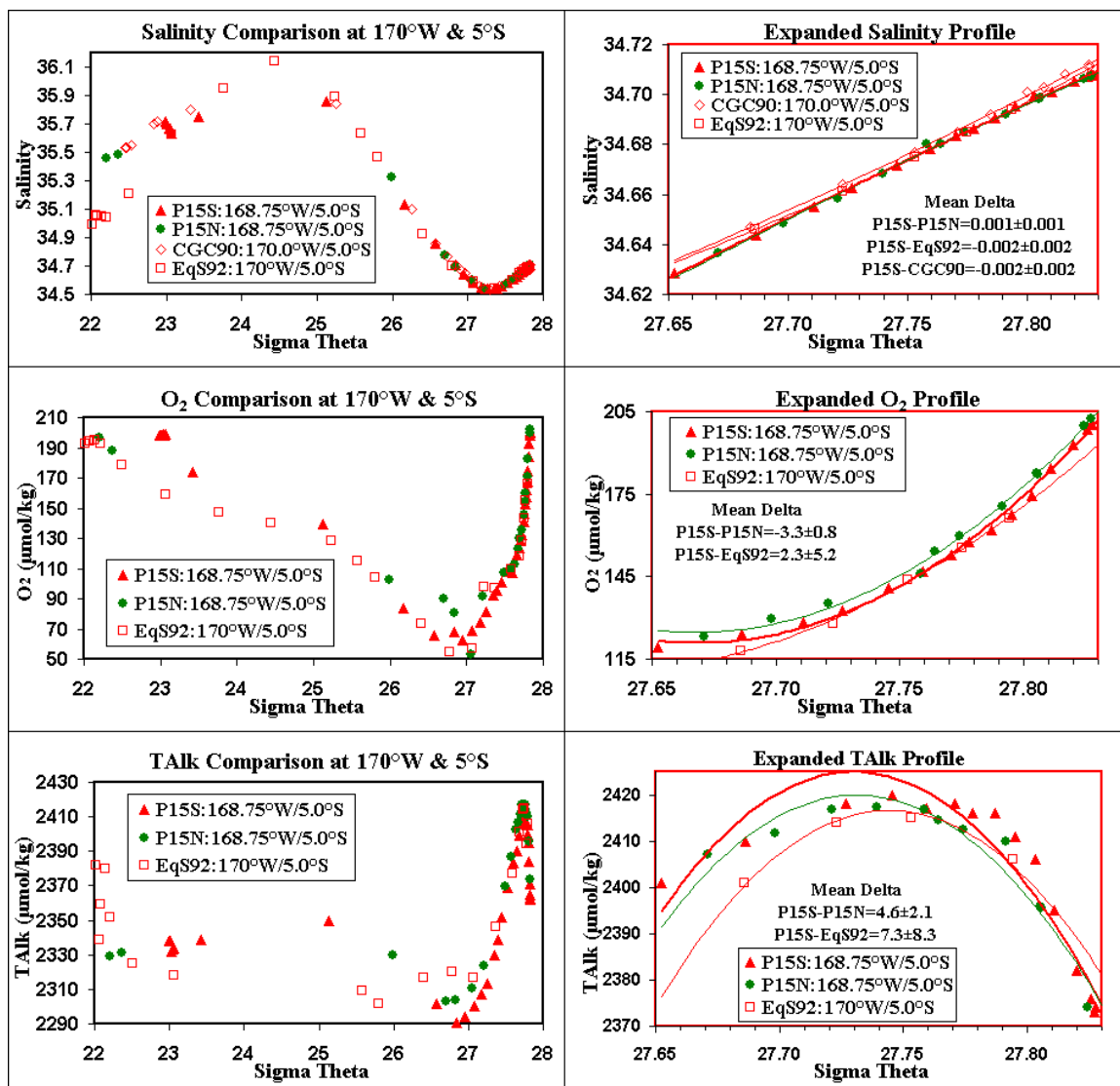


Fig. A.8a. Comparison of salinity, oxygen (O₂), and total alkalinity (TALK) at 170° W and 5° S.

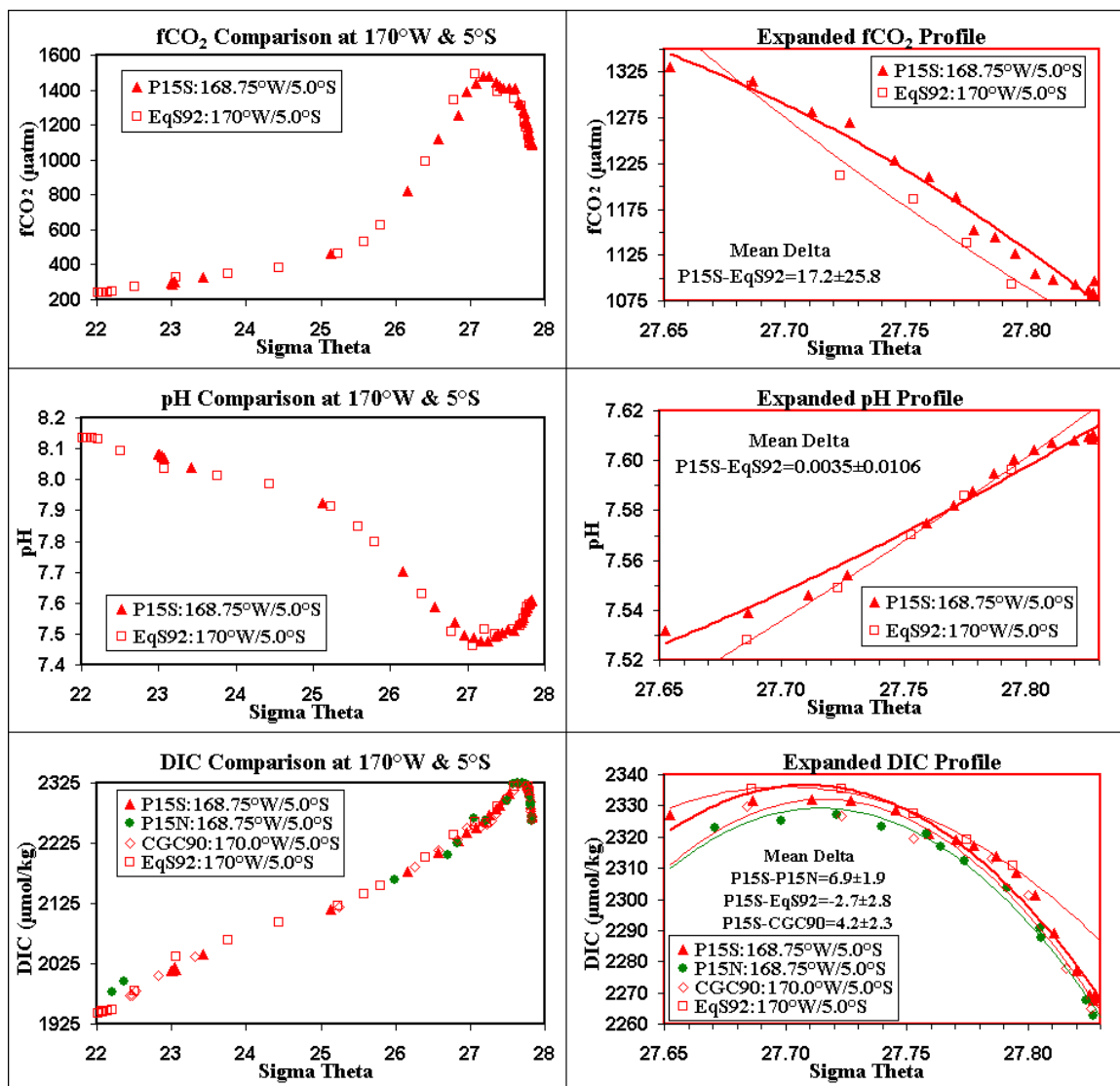


Fig. A.8b. Comparison of fugacity of CO₂ (fCO₂), pH, and dissolved inorganic carbon (DIC) at 170° W and 5° S.

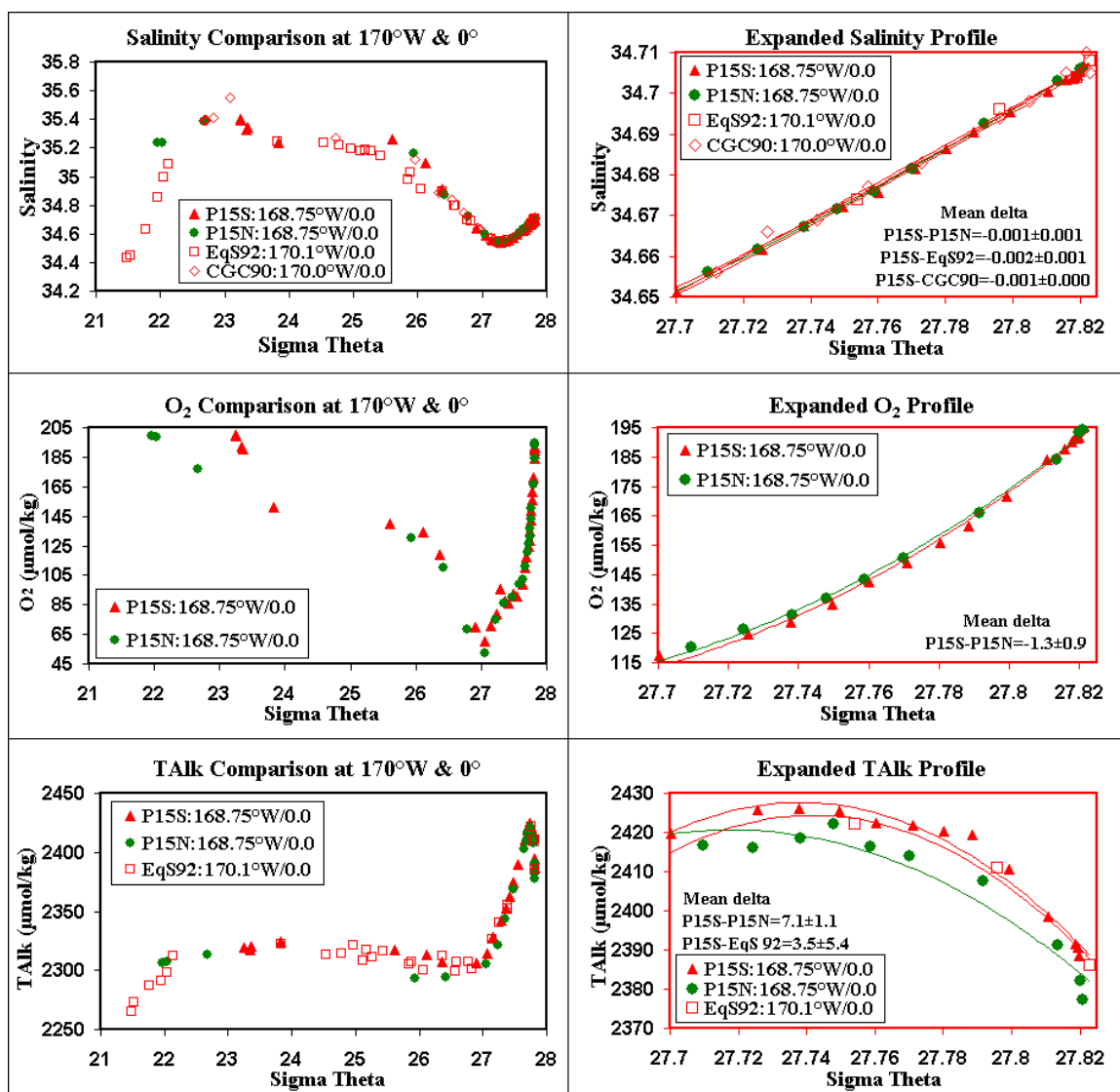


Fig. A.9a. Comparison of salinity, oxygen (O₂), and total alkalinity (TALK) at 170° W and 0°.

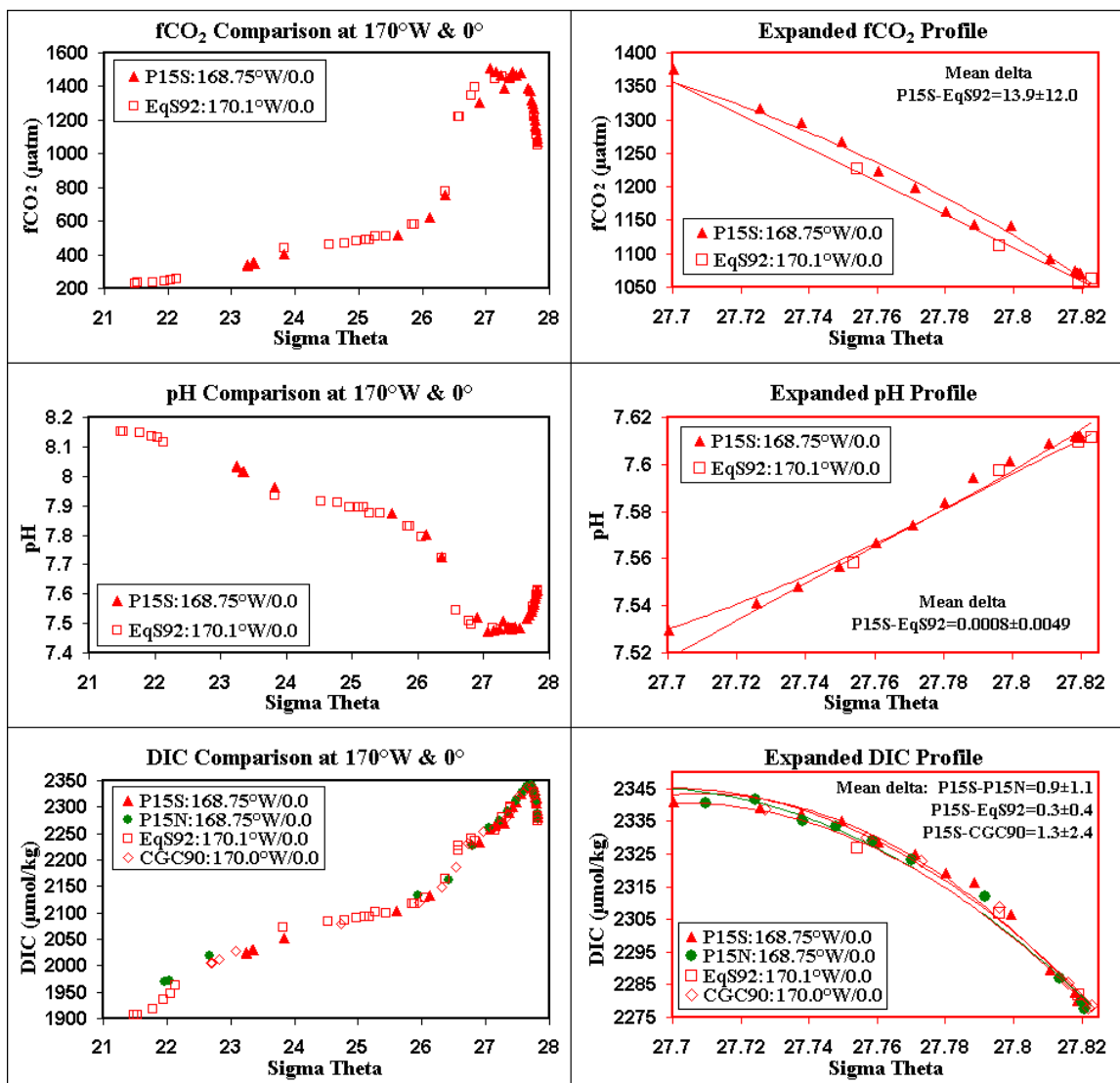


Fig. A.9b. Comparison of fugacity of CO₂ (fCO₂), pH, and dissolved inorganic carbon (DIC) at 170° W and 0°.

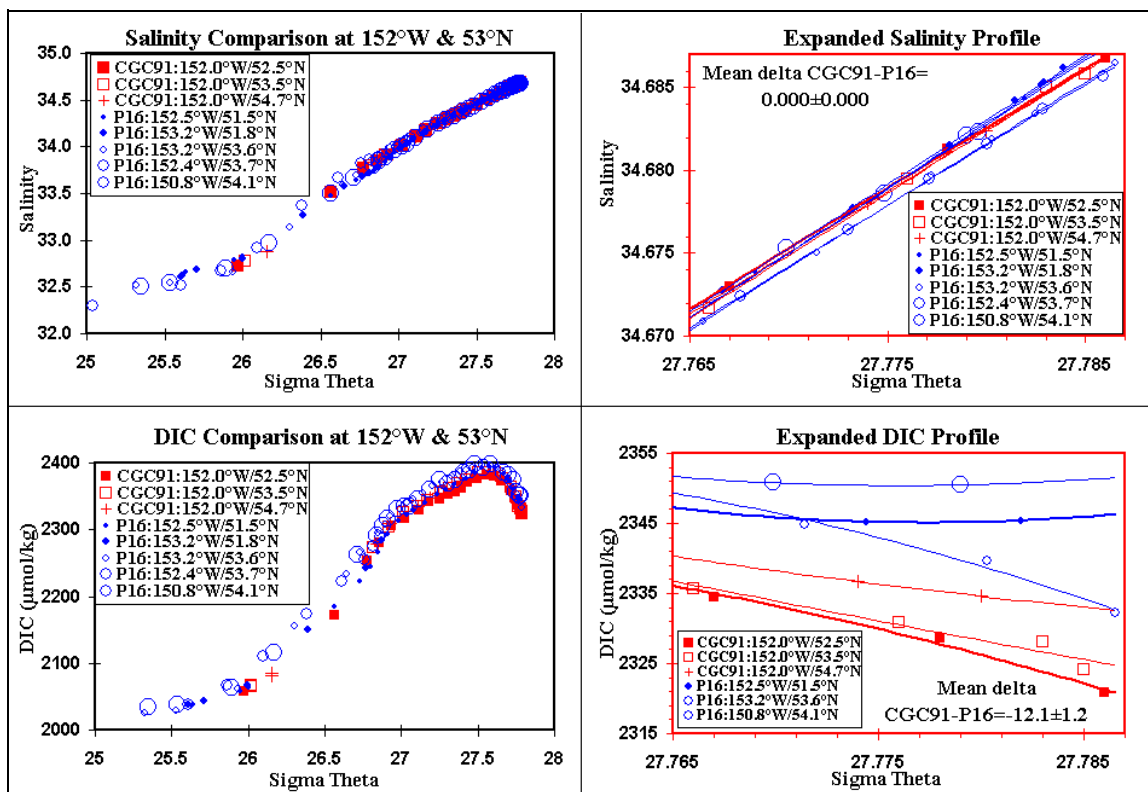


Fig. A.10. Comparison of salinity and dissolved inorganic carbon (DIC) at 152° W and 53° N.

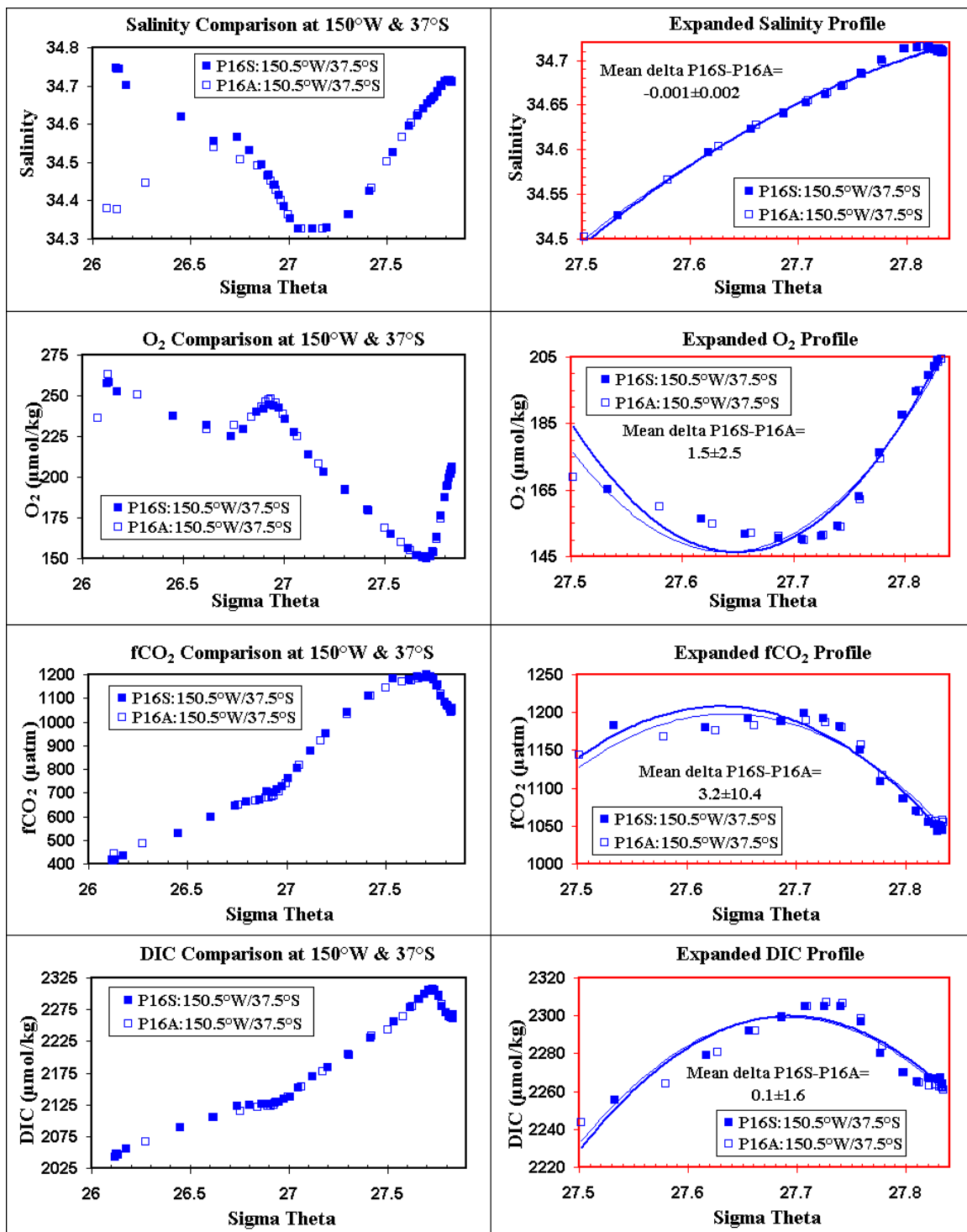


Fig. A.11. Comparison of salinity, oxygen (O₂), fugacity of CO₂ (fCO₂), and dissolved inorganic carbon (DIC) at 150° W and 37° S.

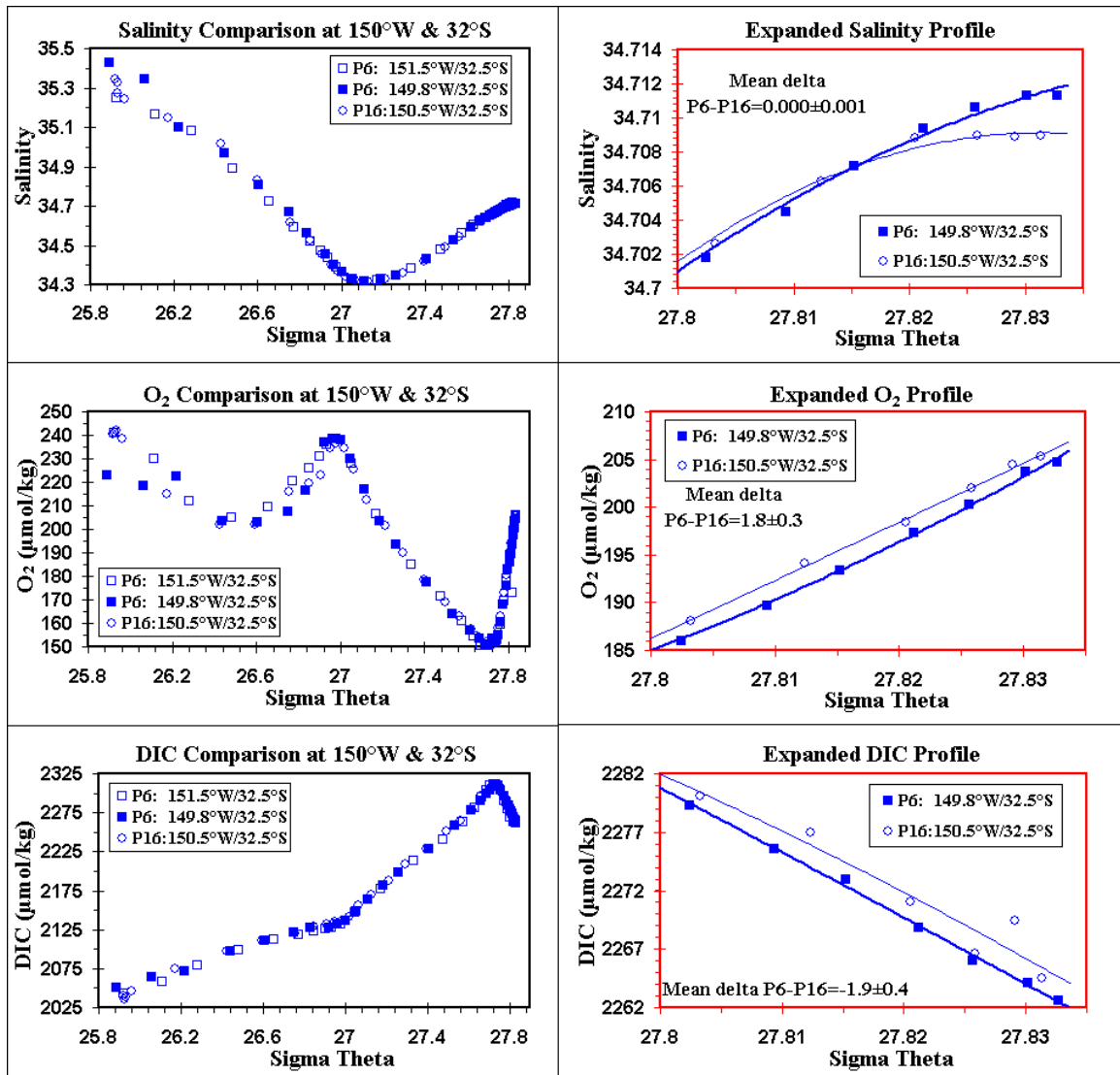


Fig. A.12. Comparison of salinity, oxygen (O₂), and dissolved inorganic carbon (DIC) at 150° W and 32° S.

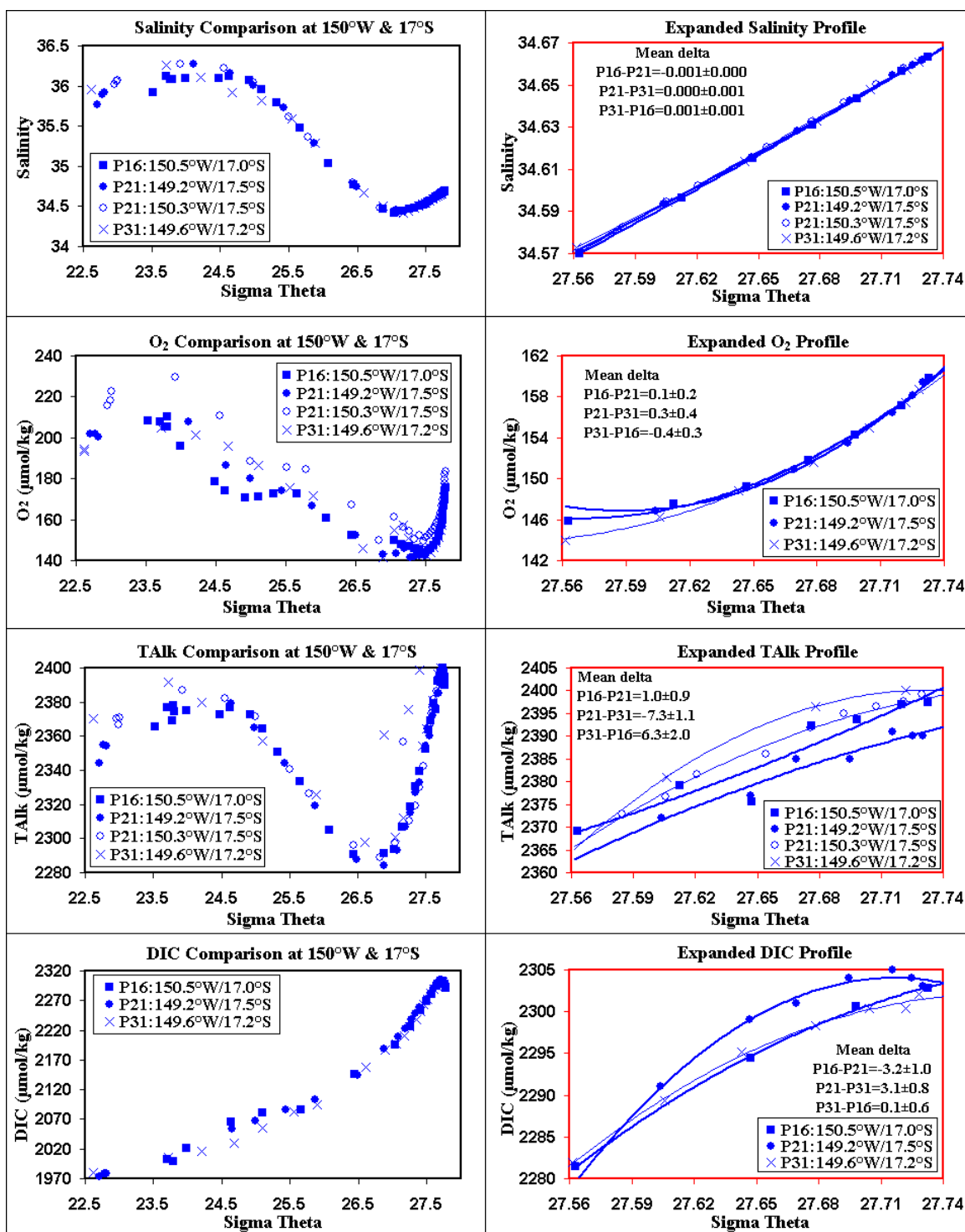


Fig. A.13. Comparison of salinity, oxygen (O₂), total alkalinity (TALK), and dissolved inorganic carbon (DIC) at 150° W and 17° S.

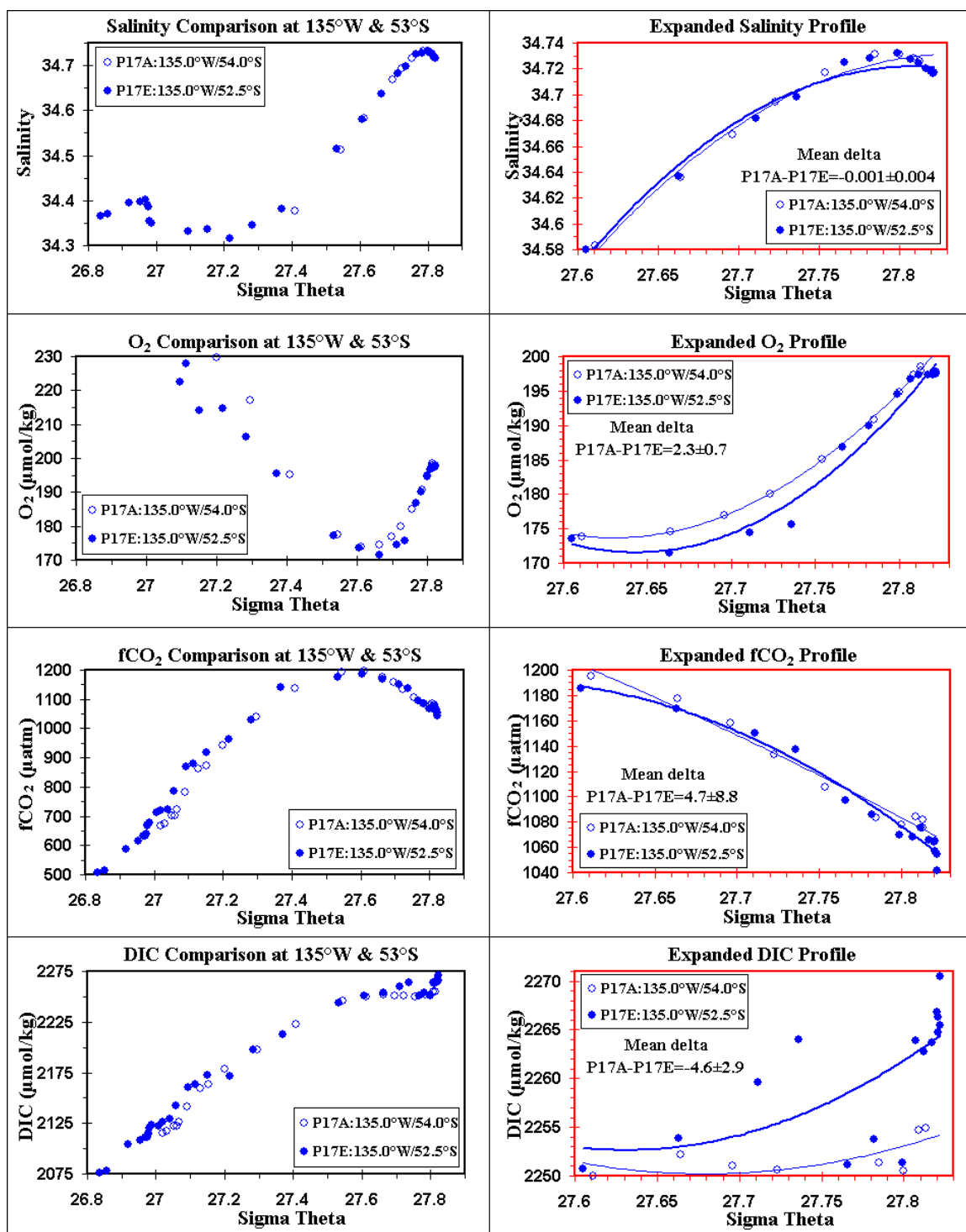


Fig. A.14. Comparison of salinity, oxygen (O₂), fugacity of CO₂ (fCO₂), and dissolved inorganic carbon (DIC) at 135° W and 53° S.

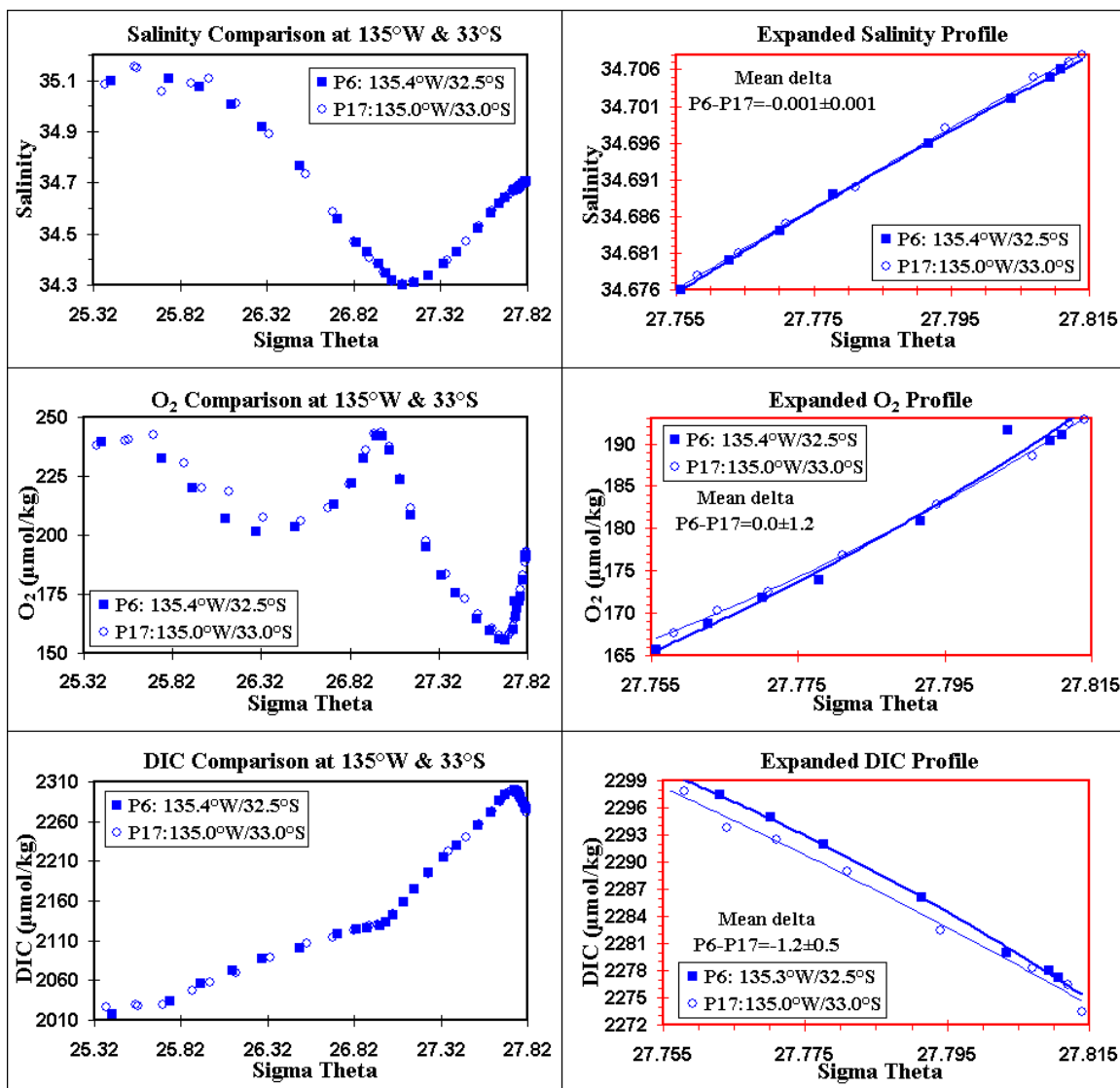


Fig. A.15. Comparison of salinity, oxygen (O₂), and dissolved inorganic carbon (DIC) at 135° W and 33° S.

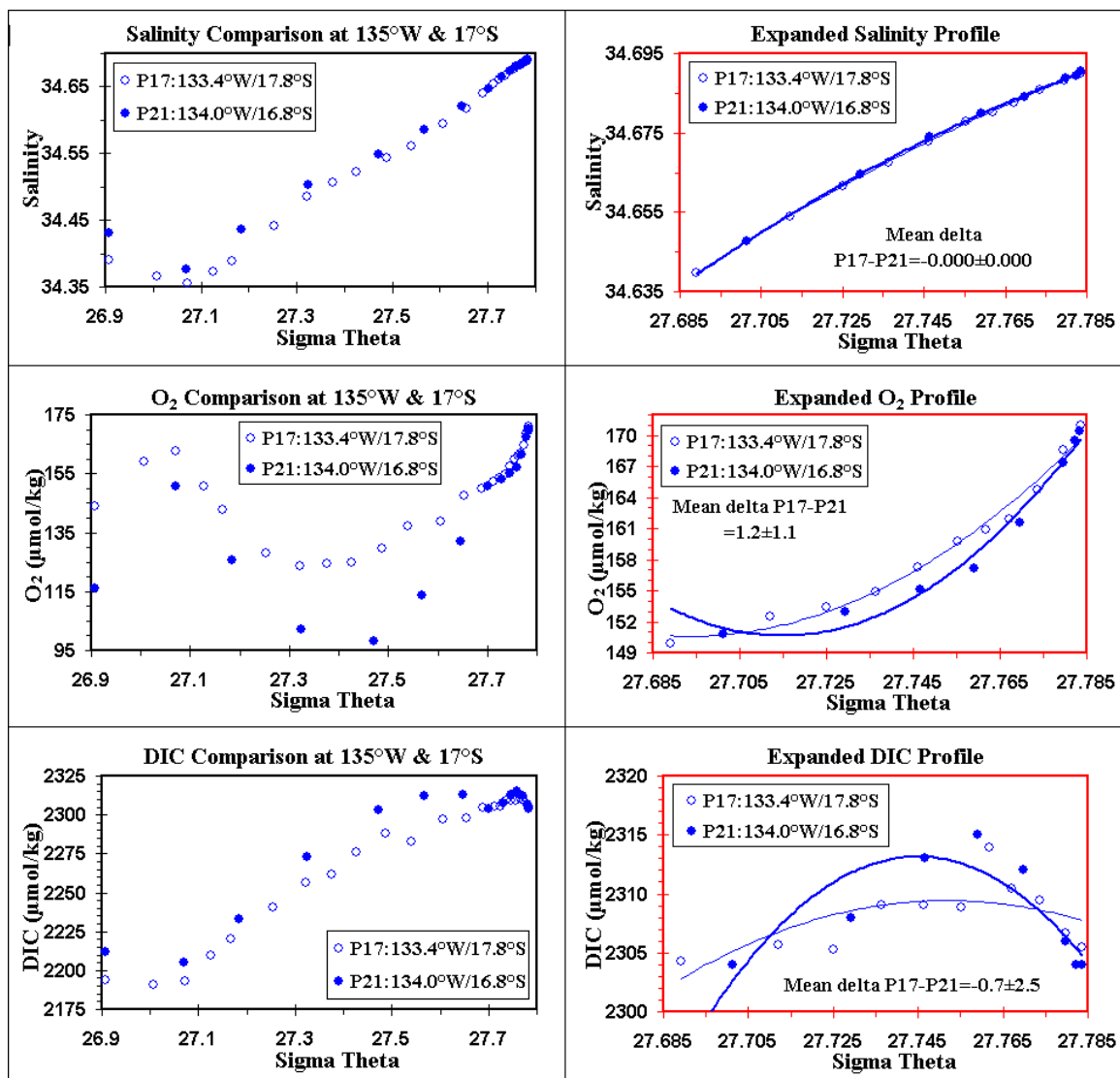


Fig. A.16. Comparison of salinity, oxygen (O₂), and dissolved inorganic carbon (DIC) at 135° W and 17° S.

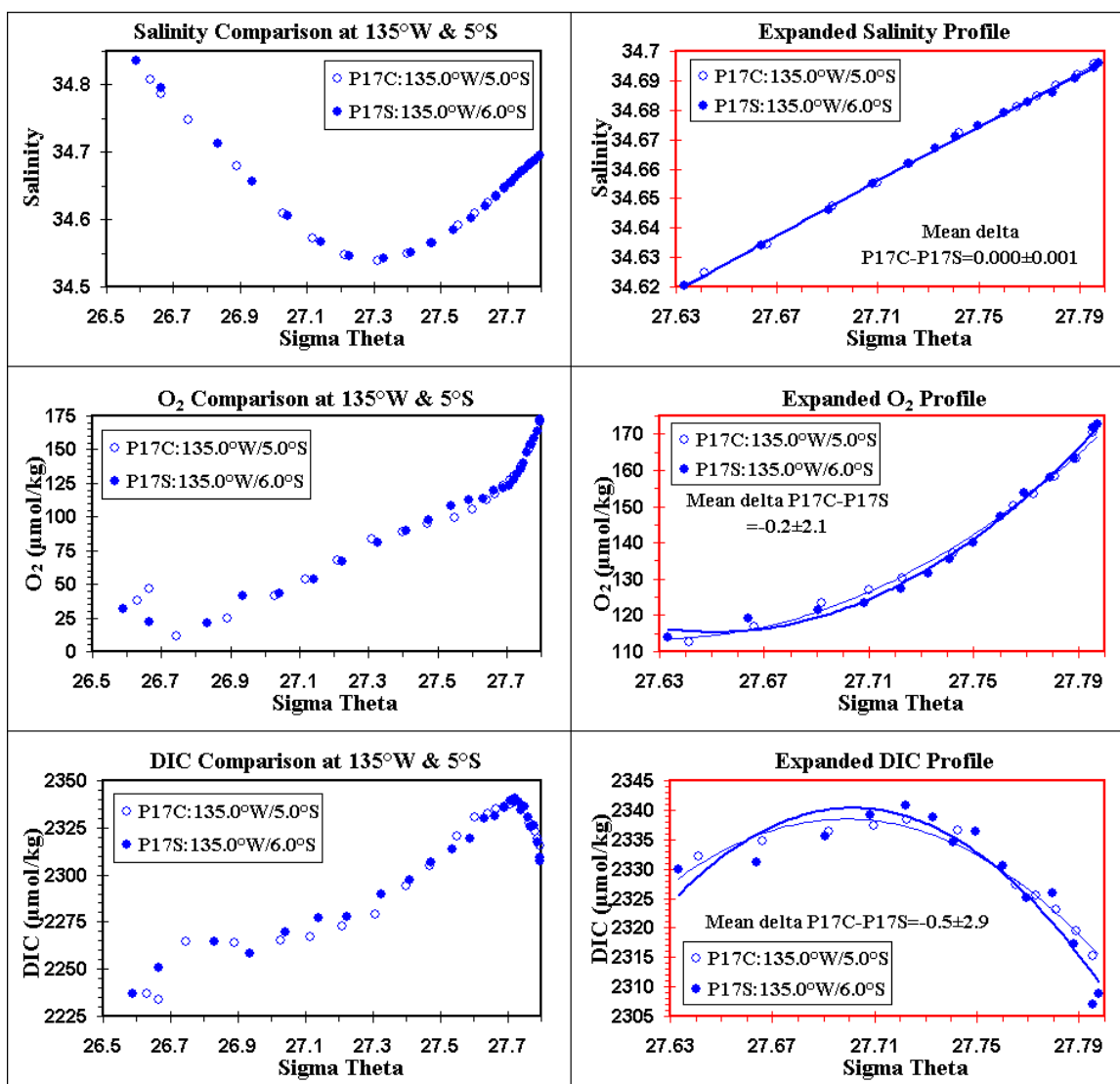


Fig. A.17. Comparison of salinity, oxygen (O₂), and dissolved inorganic carbon (DIC) at 135° W and 5° S.

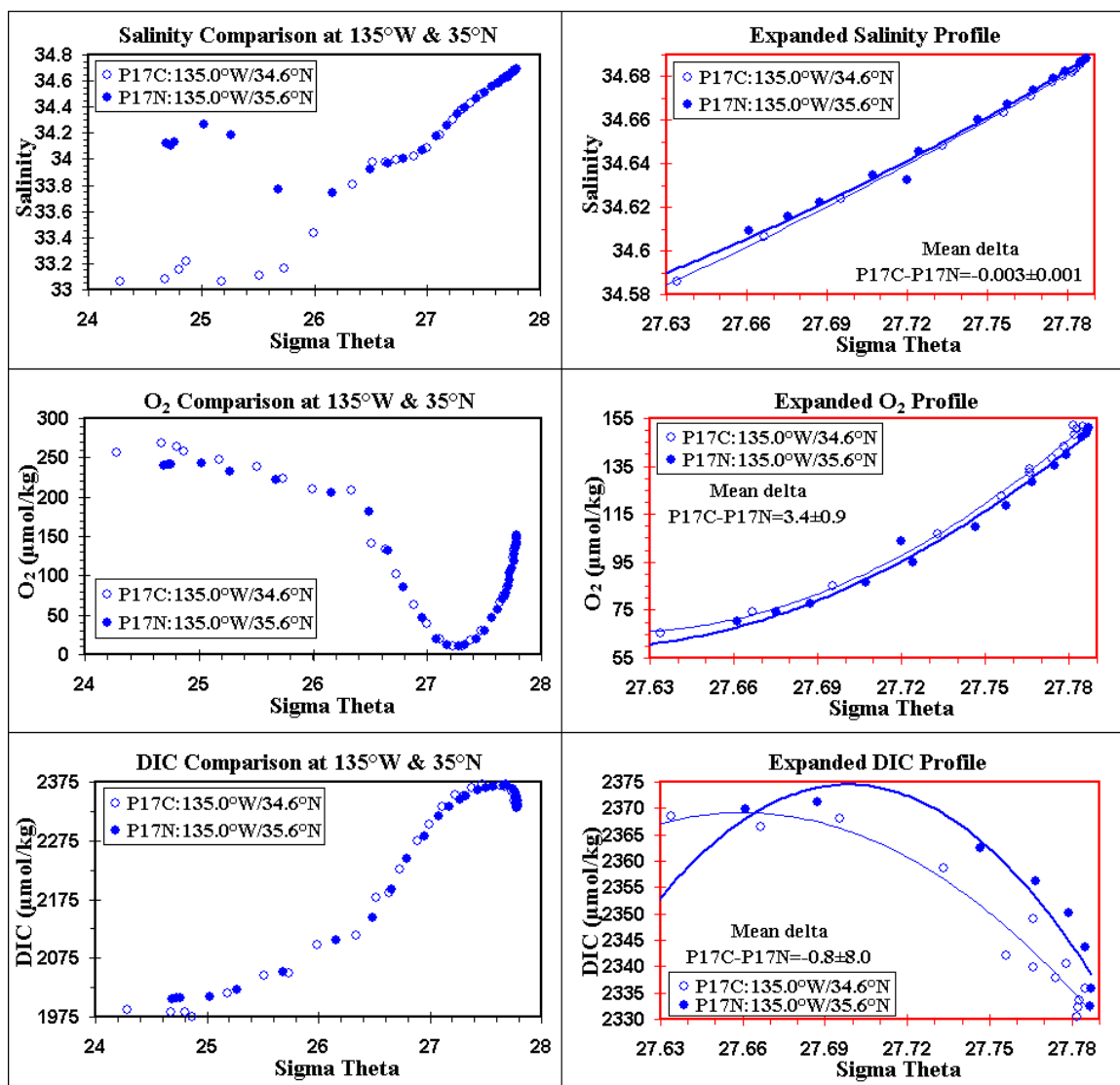


Fig. A.18. Comparison of salinity, oxygen (O₂), and dissolved inorganic carbon (DIC) at 135° W and 35° N.

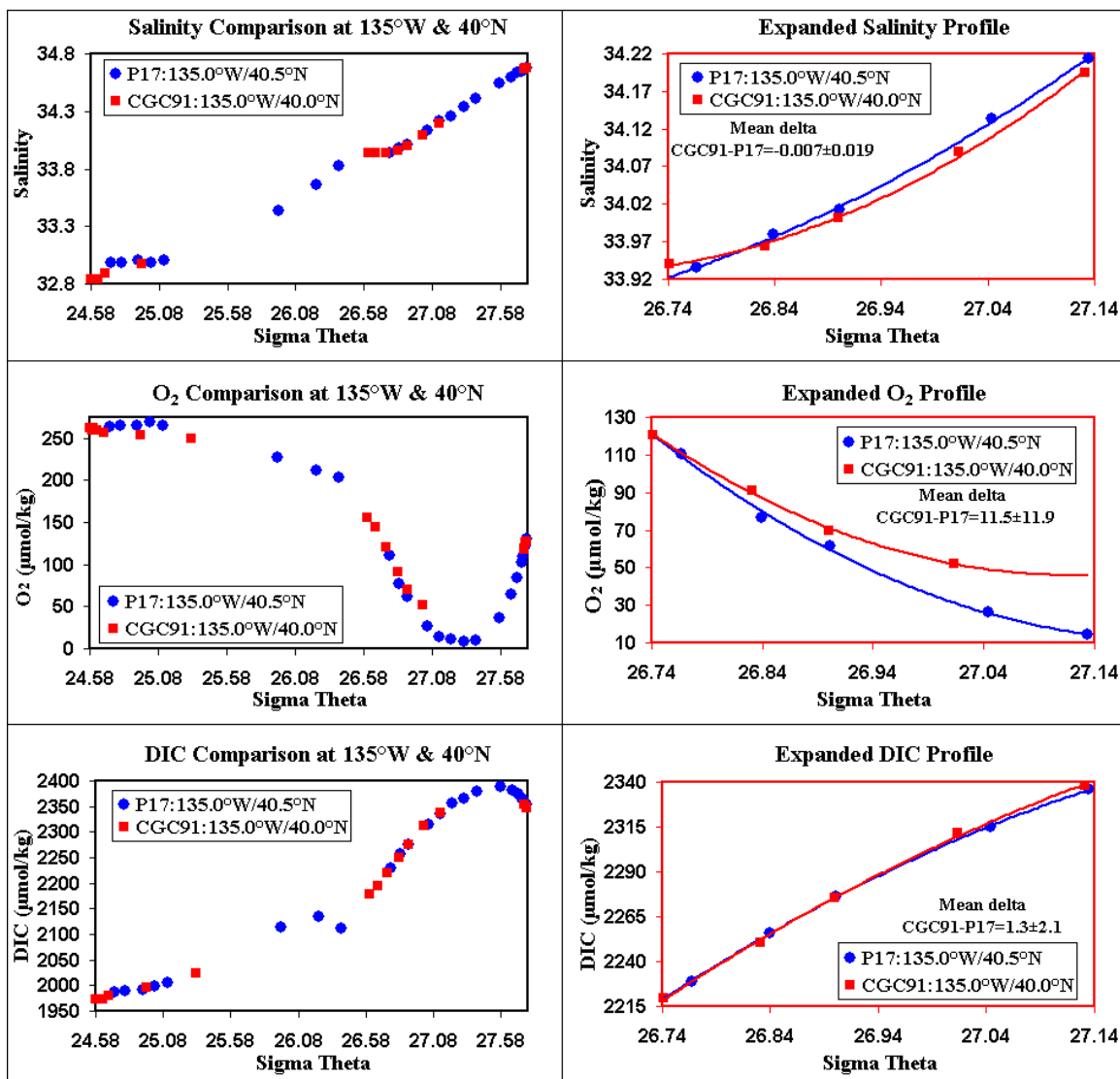


Fig. A.19. Comparison of salinity, oxygen (O₂), and dissolved inorganic carbon (DIC) at 135° W and 40° N.

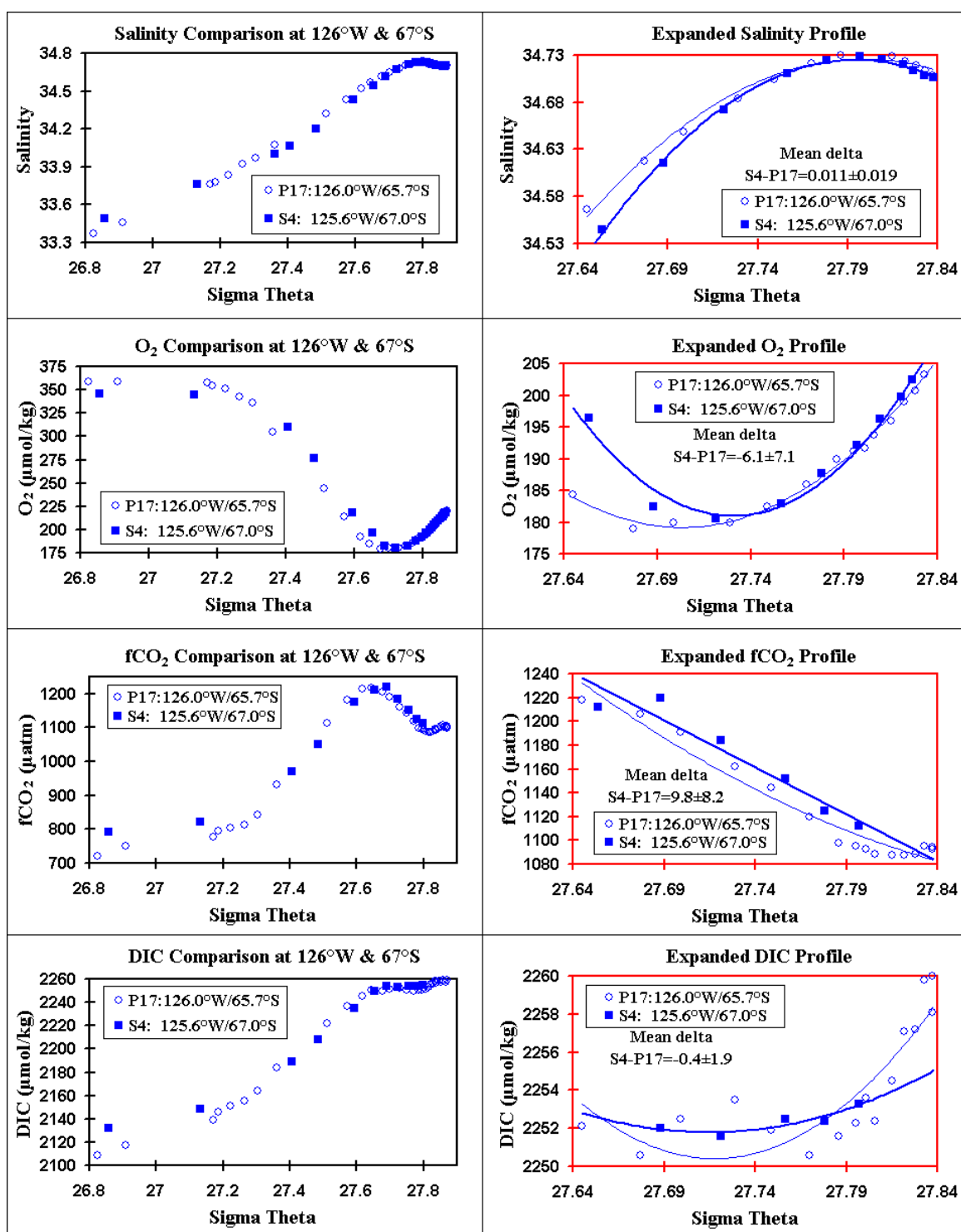


Fig. A.20. Comparison of salinity, oxygen (O₂), fugacity of CO₂ (fCO₂), and dissolved inorganic carbon (DIC) at 126° W and 67° S.

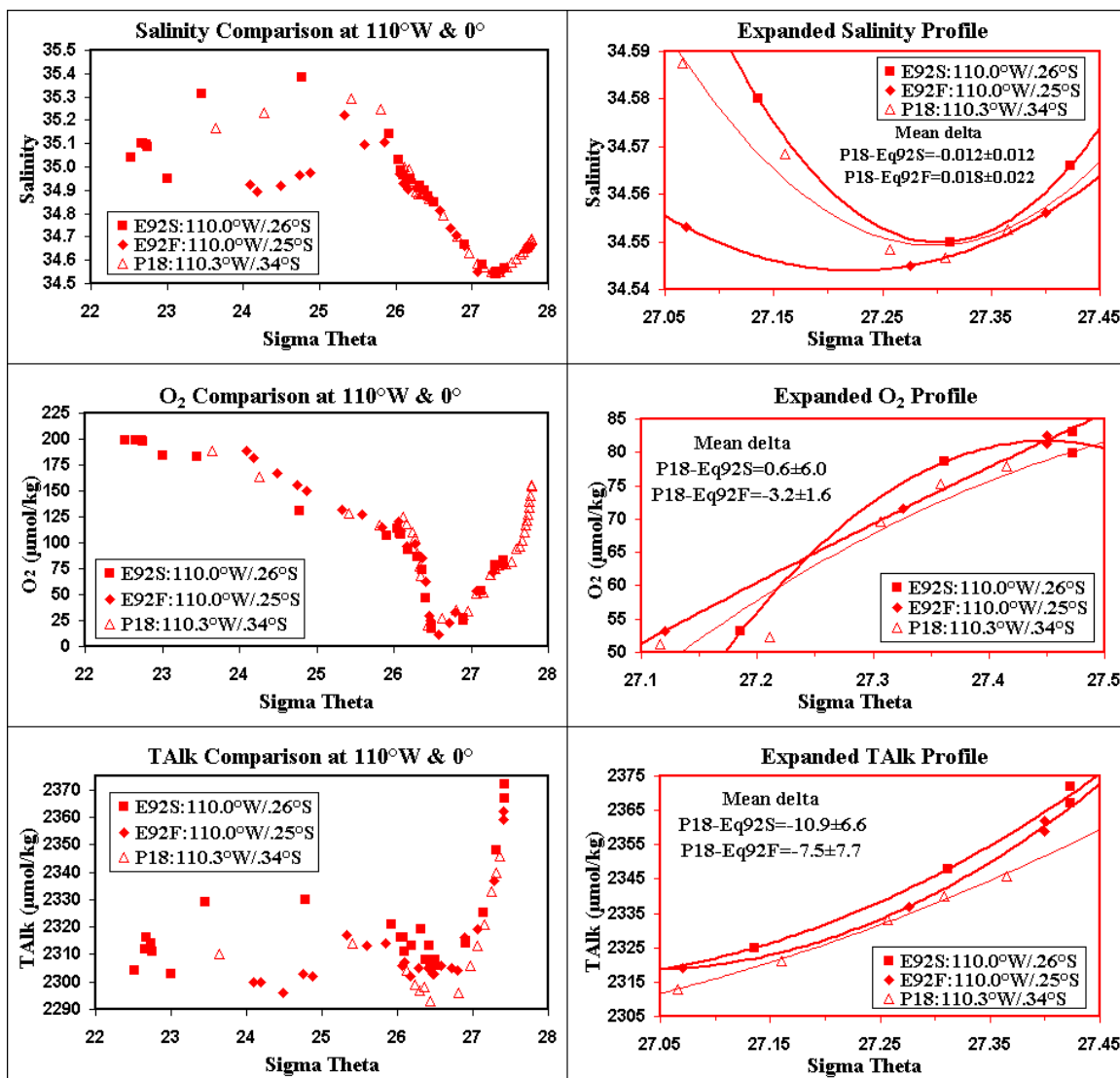


Fig. A.21a. Comparison of salinity, oxygen (O₂), and total alkalinity (TALK) at 110° W and 0°.

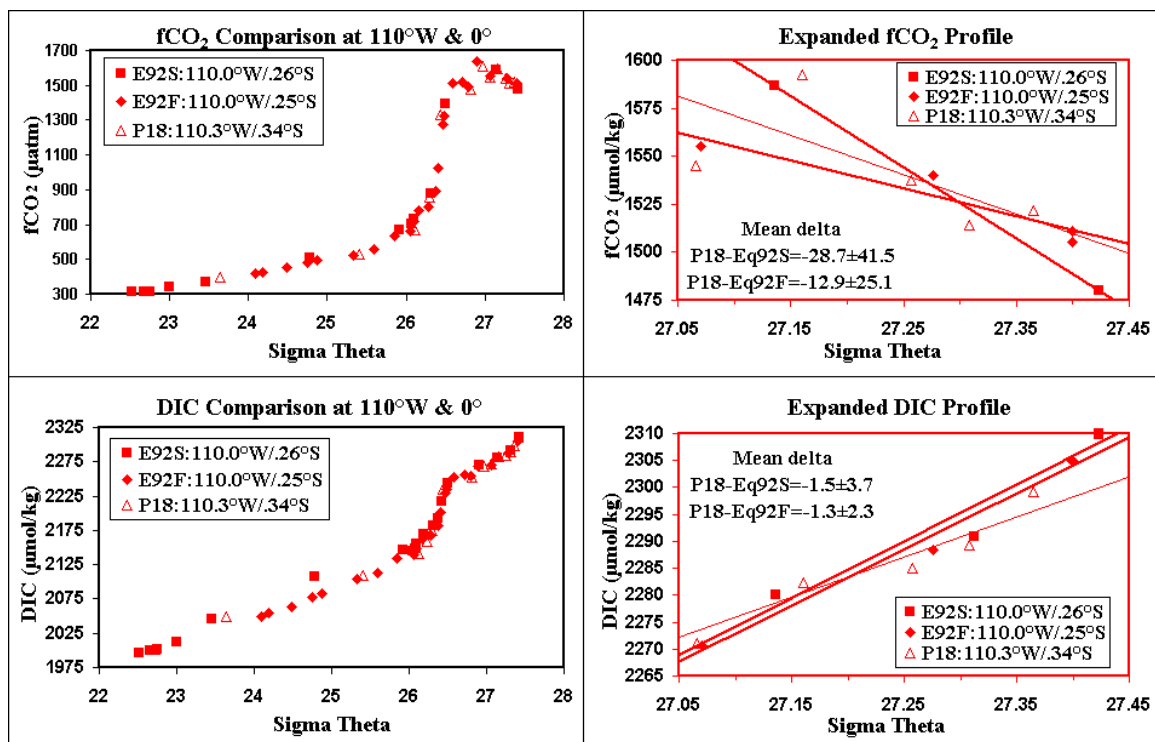


Fig. A.21b. Comparison of fugacity of CO₂ (fCO₂) and dissolved inorganic carbon (DIC) at 110° W and 0°.

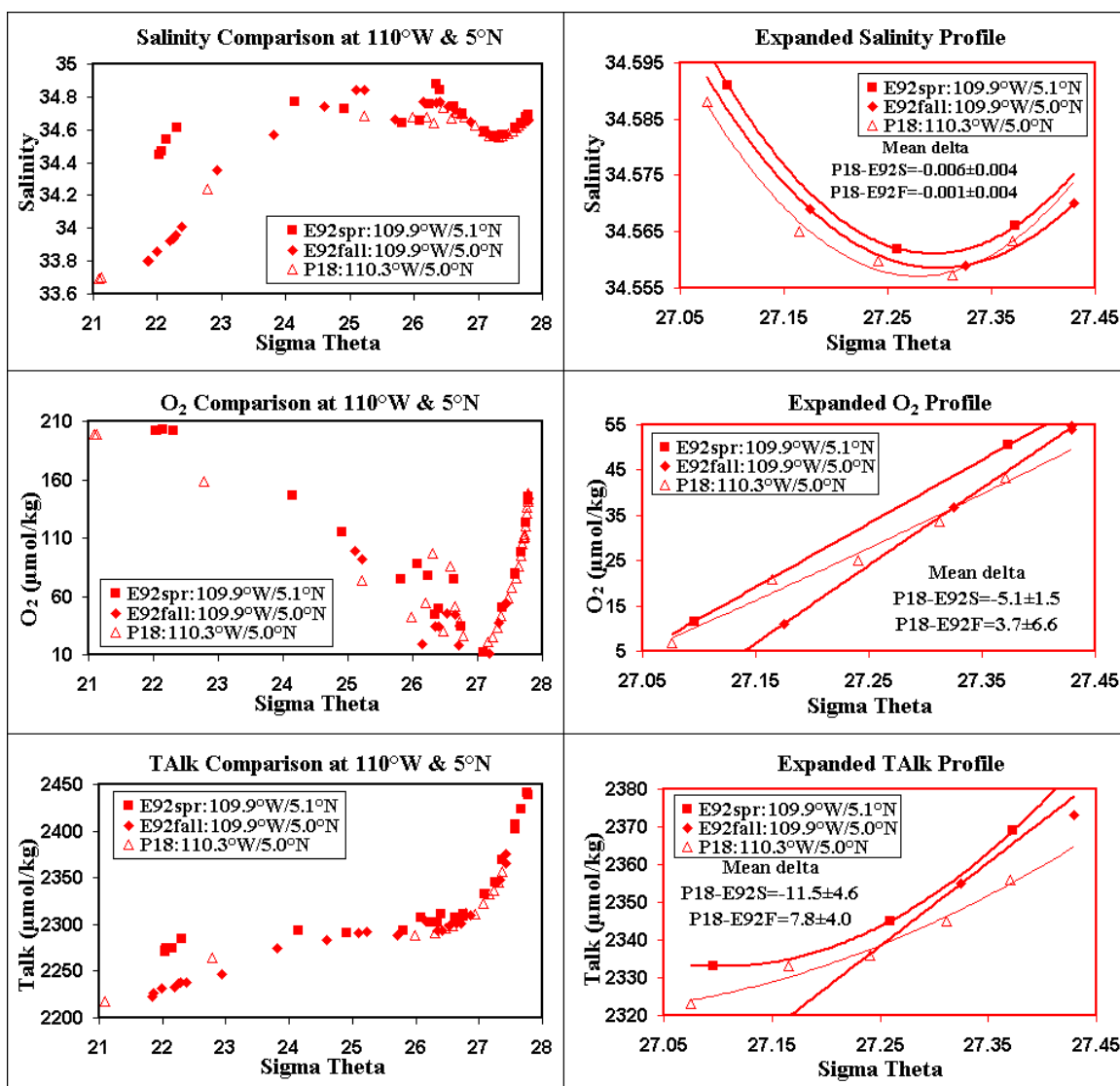


Fig. A.22a. Comparison of salinity, oxygen (O₂), and total alkalinity (TALK) at 110° W and 5° N.

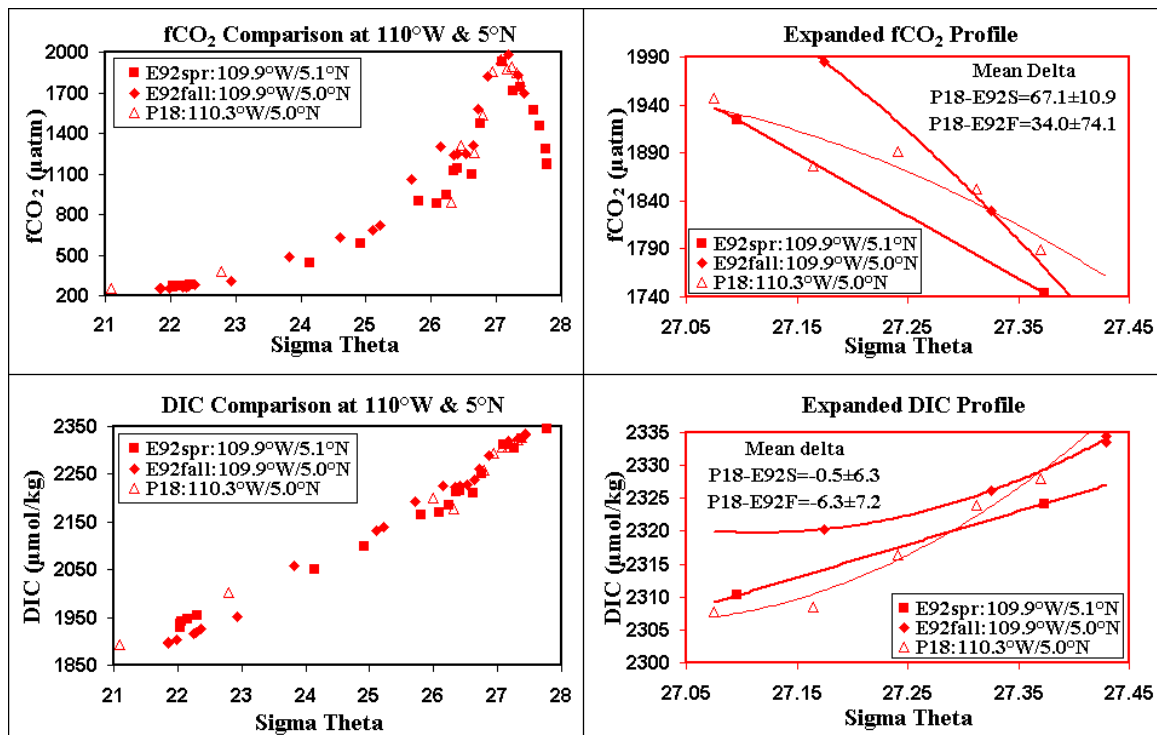


Fig. A.22b. Comparison of fugacity of CO₂ (fCO₂) and dissolved inorganic carbon (DIC) at 110° W and 5° N.

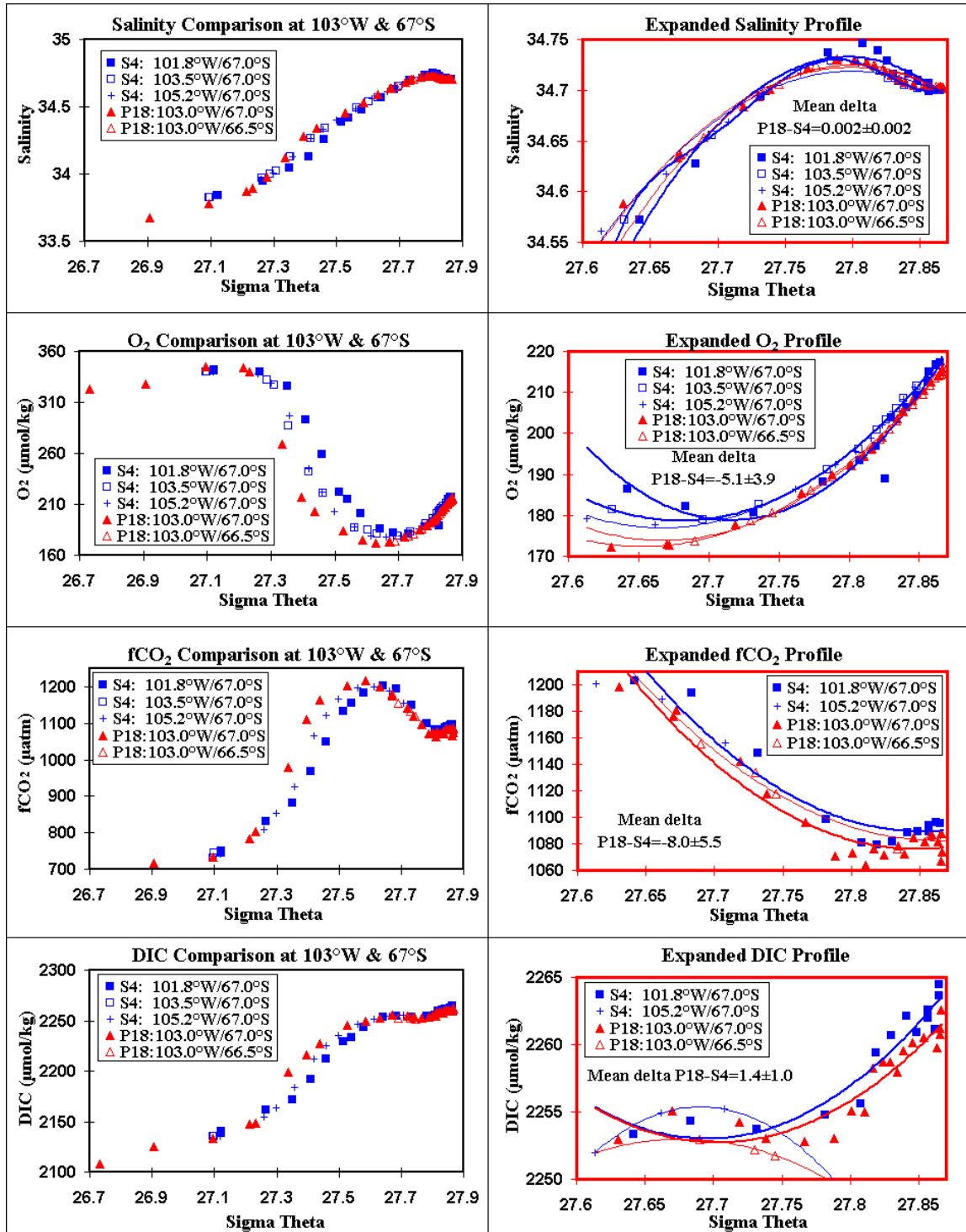


Fig. A.23. Comparison of salinity, oxygen (O₂), fugacity of CO₂ (fCO₂), and dissolved inorganic carbon (DIC) at 103° W and 67° S.

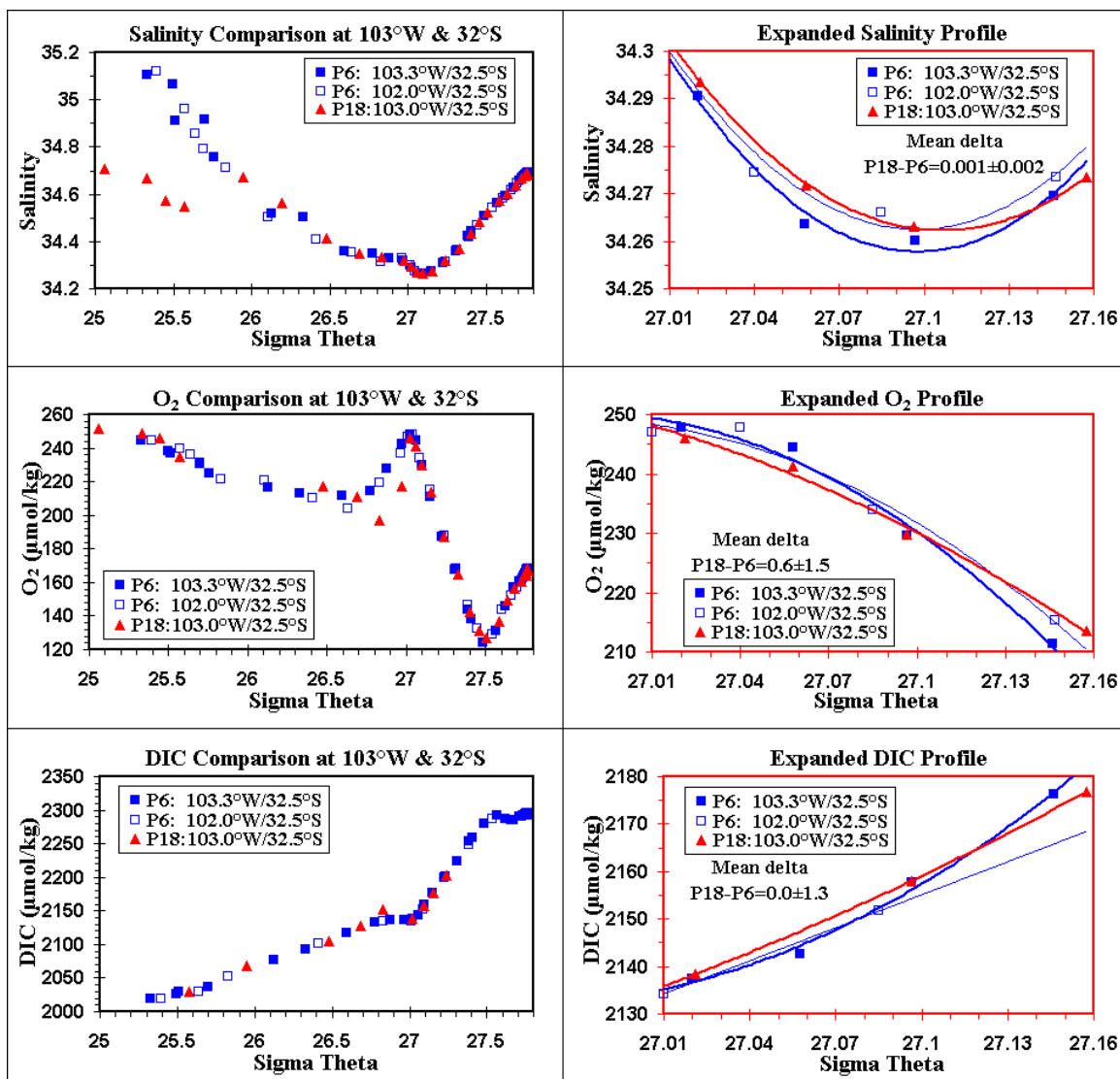


Fig. A.24. Comparison of salinity, oxygen (O₂), and dissolved inorganic carbon (DIC) at 103° W and 32° S.

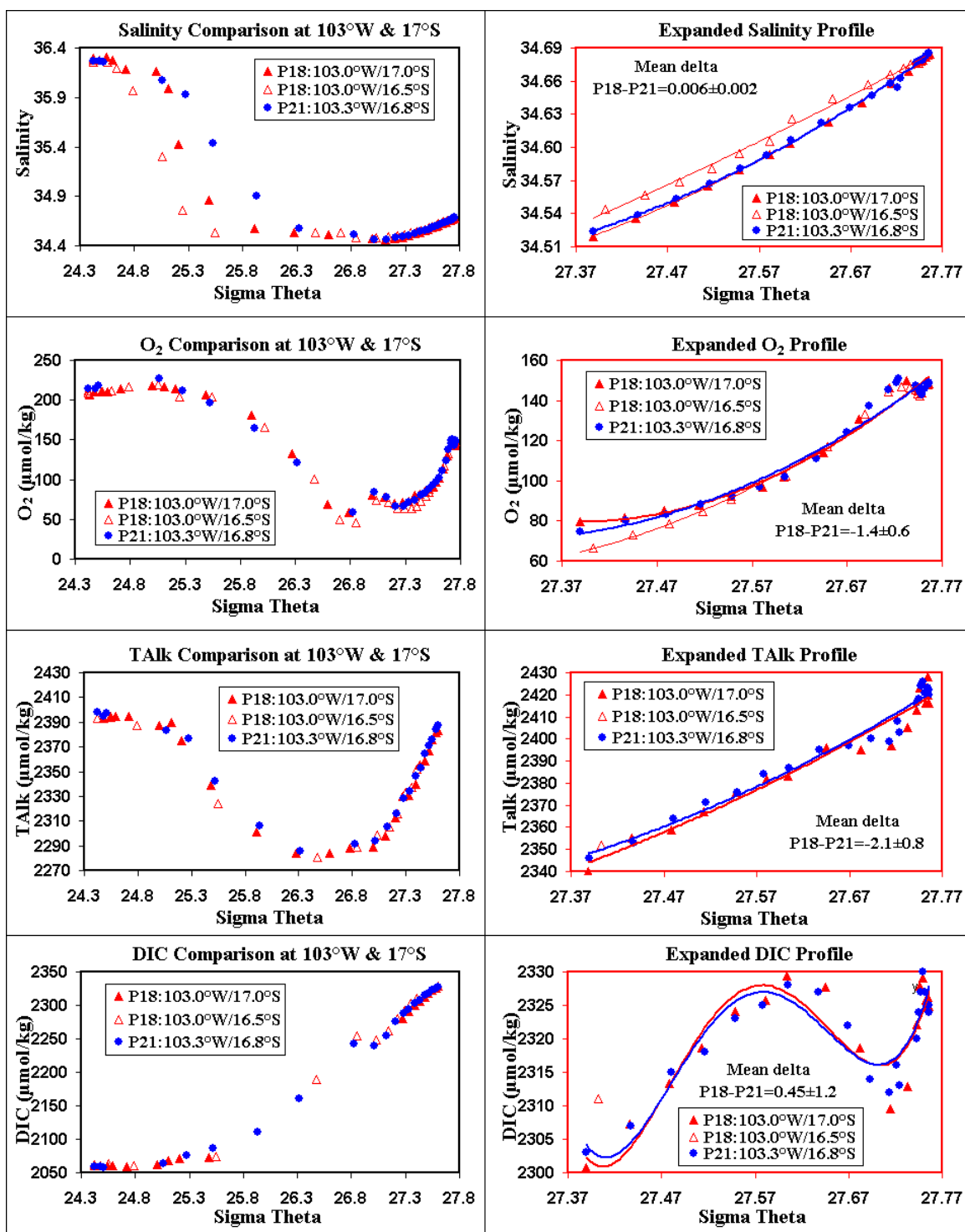


Fig. A.25. Comparison of salinity, oxygen (O₂), total alkalinity (TALK), and dissolved inorganic carbon (DIC) at 103° W and 17° S.

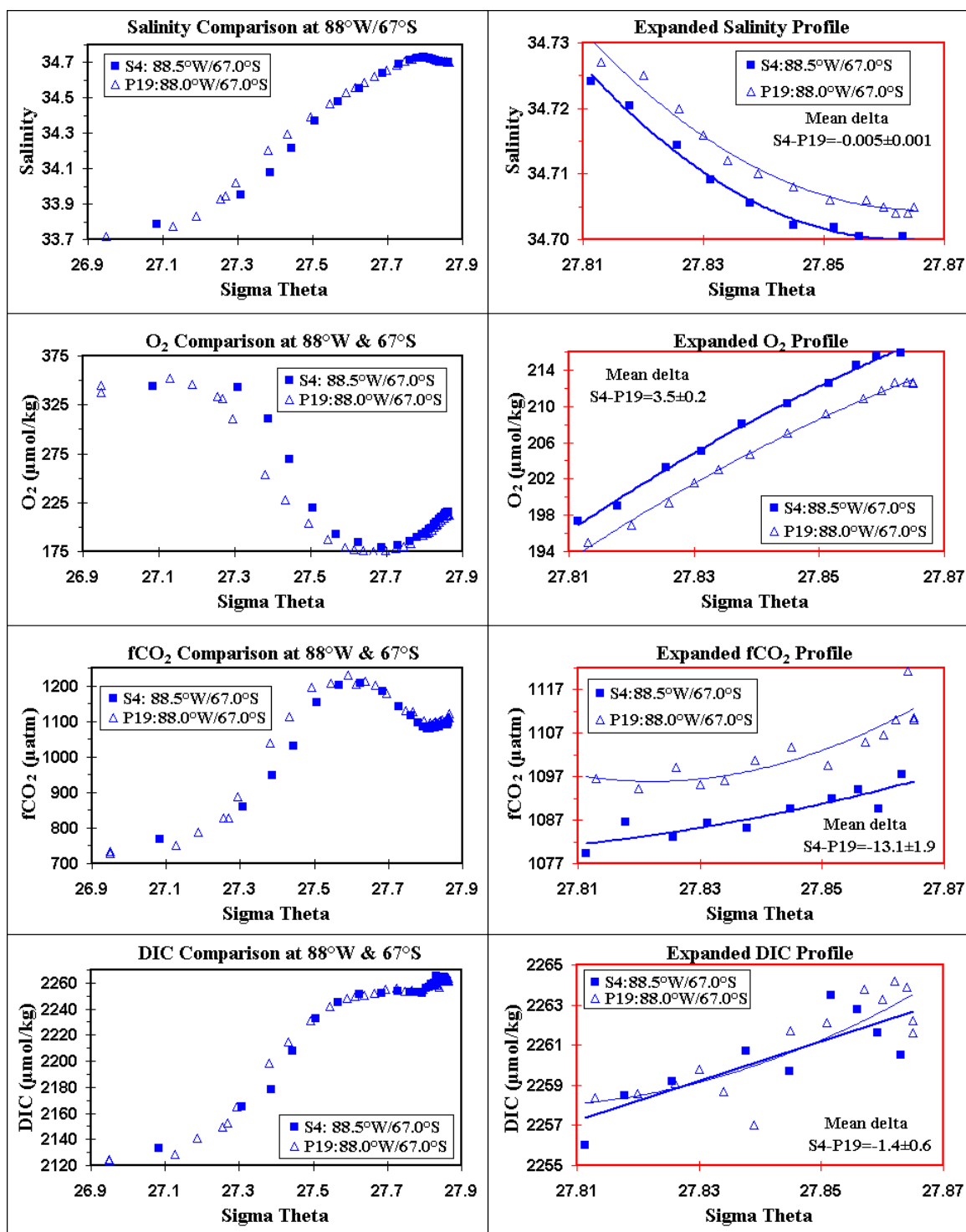


Fig. A.26. Comparison of salinity, oxygen (O₂), fugacity of CO₂ (fCO₂), and dissolved inorganic carbon (DIC) at 88° W and 67° S.

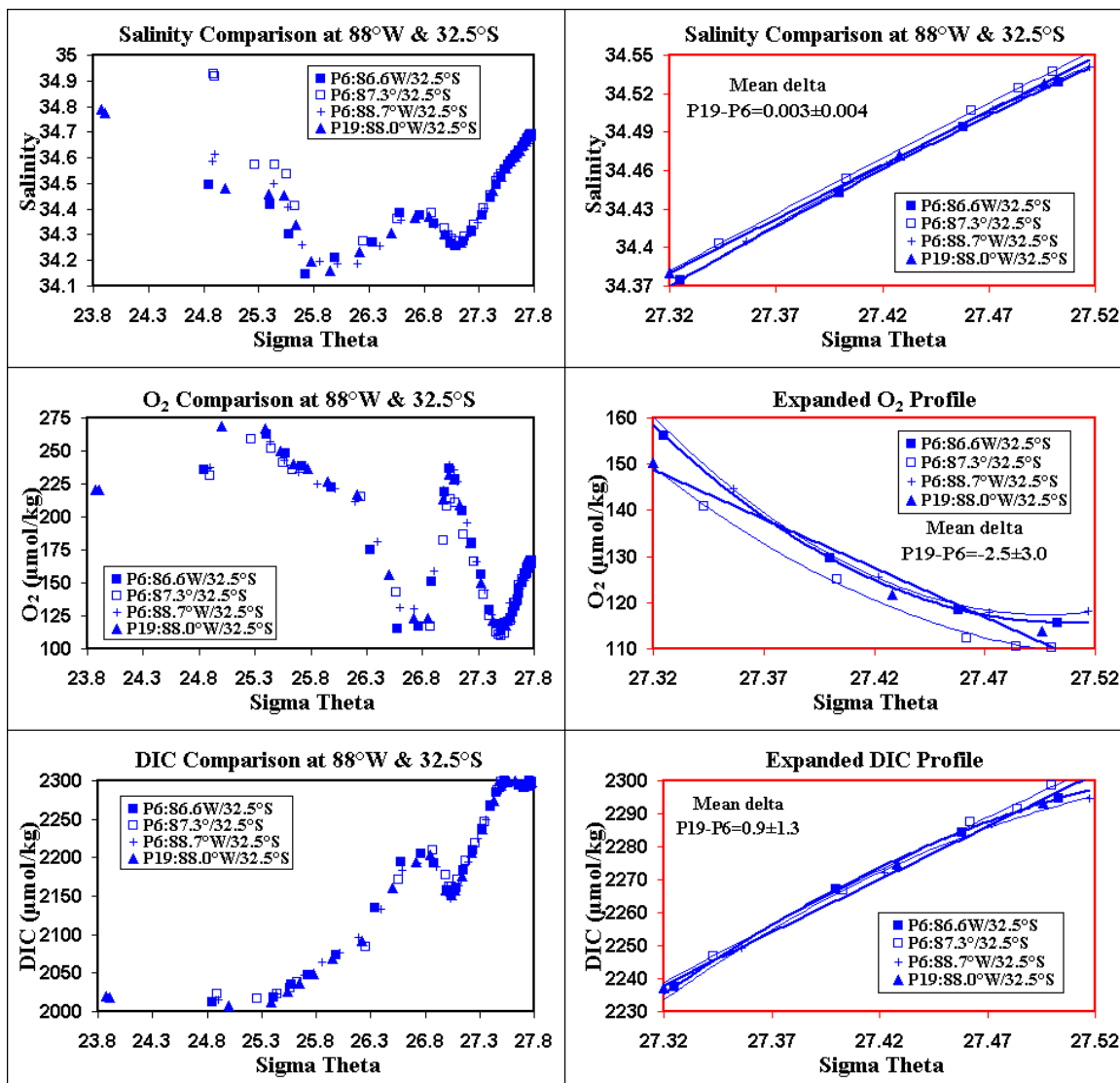


Fig. A.27. Comparison of salinity, oxygen (O₂), and dissolved inorganic carbon (DIC) at 88° W and 32° S.

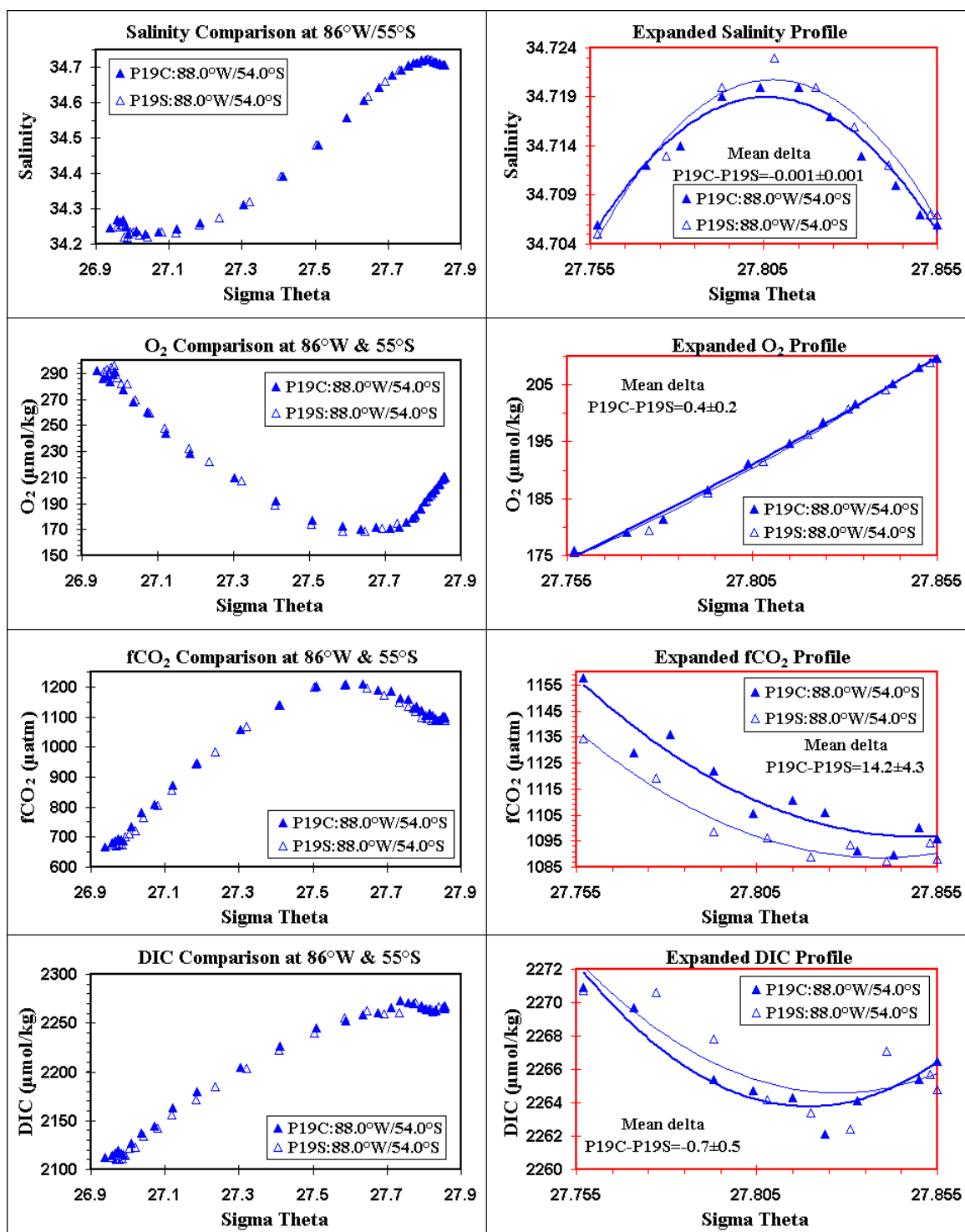


Fig. A.28. Comparison of salinity, oxygen (O₂), fugacity of CO₂ (fCO₂), and dissolved inorganic carbon (DIC) at 86° W and 55° S.

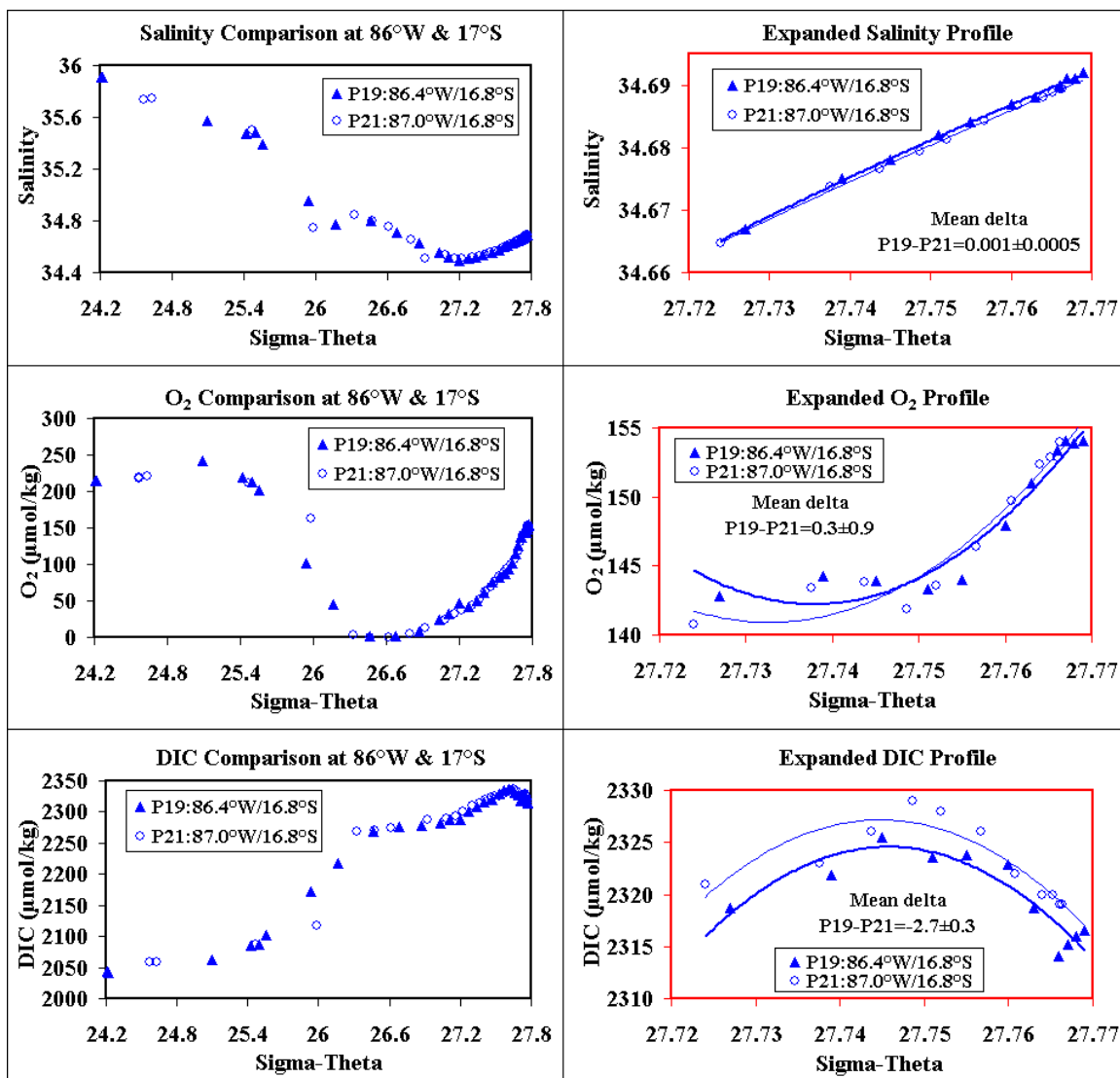


Fig. A.29. Comparison of salinity, oxygen (O₂), and dissolved inorganic carbon (DIC) at 86° W and 17° S.

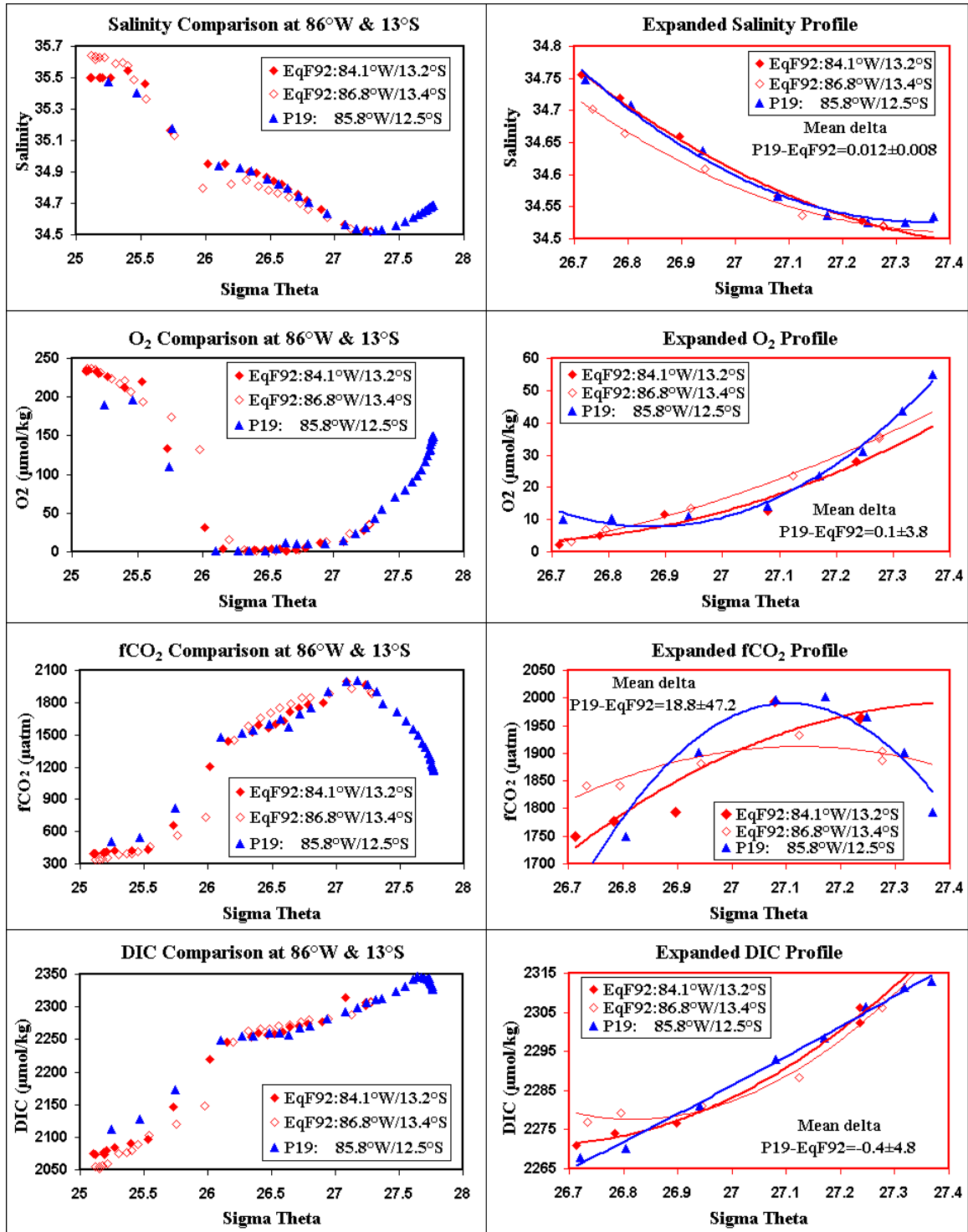


Fig. A.30. Comparison of salinity, oxygen (O₂), fugacity of CO₂ (fCO₂), and dissolved inorganic carbon (DIC) at 86° W and 13° S.